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THE

PHYSICAL REVIEW.

THE MOBILITIES OF ELECTRONS IN HYDROGEN.

By Leonard B. Loeb.

Synopsis.

Electron mobilities in pure hydrogen have been measured for pressures of 73 to 635 mm., using a modified alternating field method with fields up to 70 volts/cm. Undamped oscillation of 15,000 to 200,000 cycles were obtained from a vacuum tube oscillator and were measured with a precision wave-meter. By using a constant retarding potential of 6 volts the disturbing effect of ions of impurities was eliminated and curves without the usual feet were obtained. The mobility (reduced to a pressure of 76 cm.) is found to be best represented by the equation: $k = 2.74 \times 10^6 / [399 + (Vo/d)(760/p^{3/4}]$, where Vo/d is the critical field in volts per cm. and p is the pressure in mm. *Comparison with kinetic theory.* This equation is practically of the same form as that found by less accurate measurements for nitrogen and since it differs from Townsend's theoretical equation: $k = a/[b + (Vo/d)(760/p)]^{1/2}$, either the mean free path of the electron or its loss of energy at impact are probably functions of the velocity of the electron. When the electrical fields are small the mobility at atmospheric pressure comes out 68.6 *m*/sec. whereas the kinetic theory gives 130.6; hence the actual *mean free path* must be only about half that assumed by the theory.

In a recent paper[1] the writer showed that by applying the high-frequency oscillations of an audion oscillator to the Rutherford alternating current method of mobility measurement, it was possible to determine electron mobilities in pure N_2 whose values were much higher than any previously obtained. The investigations in N_2 have been extended to H_2 with a considerable improvement in the technique, and it is the purpose of this paper to report the progress made.

The technique of measurement was improved along the following lines:

1. By the use of a new oscillating circuit which gave undamped oscillations whose amplitude could be varied at will without changing their frequency.

2. By the elimination of the asymptotic feet of the mobility curves through the use of a small retarding field of constant value. This field acted by removing the ions formed through the attachment of electrons to molecules of impurities.

3. By the elimination of the disturbing effect due to a gradual con-

tamination of the gas by impurities. These impurities were presumably liberated from the walls of the containing vessel on standing. The effect of the impurities was avoided by introducing fresh gas into the chamber before each set of readings.

4. By the use of a precision wave meter accurately covering the whole range of frequencies worked with in place of the rough instrument first employed.

1. The new oscillating circuit employed is shown in Fig. 1. The

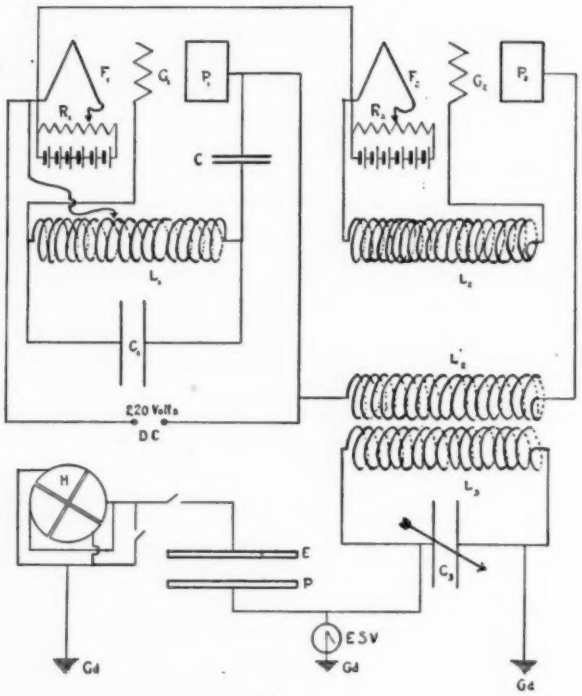


FIG. 1

primary oscillations were set up in the system $C_1L_1F_1G_1P_1$, where the frequency is once and for all determined by the inductance L_1 and the capacity C_1. The oscillators $F_1C_1P_1$ were two Western Electric Company "E" tubes acting in parallel. The filament current and the plate resistance were always kept constant. The secondary inductance L_2, closely coupled to L_1, took the oscillations from it and thus placed an oscillating potential difference of the frequency of that in the primary circuit between the filament F_2 and the grid G_2 of a secondary "E" tube oscillator, $F_2G_2P_2$. The steady electron current from F_2 to G_2 driven by 200 volts direct current was therefore periodically interrupted by the oscillations in the primary circuit. A series of unidirectional

current surges accordingly passed through the inductance L_2'. These acted on the inductance L_3 of the tertiary system L_3C_3 which was closely coupled to L_2'. Thus (when L_3C_3 was tuned to resonance with the primary system), there were set up across the condenser C_3 a continuous train of undamped oscillations. The inductance and capacity L_3 and C_3 were chosen to be as nearly the same as L_1 and C_1 as possible, the final sharp tuning being accomplished by a small variable air condenser in parallel with C_3. The amplitude of the oscillations in the system C_3L_3 was varied by varying the energy in the secondary circuit. This was accomplished by changing the secondary filament current through F_2 by varying R_2. One side of the condenser C_3 was grounded and the other side was connected to the plate source of electrons used in mobility measurement. The potential differences obtained across C_3 varied from 10 to 140 volts and were measured on two Kelvin electrostatic voltmeters. These were calibrated against a standard current voltmeter after each mobility determination. The frequencies used in these measurements varied from 15,000 to 200,000 cycles per second. To cover this range of frequencies and voltages it was necessary to use three sets of the inductances L_1, L_2, L_2' and L_3, each set having values of about 4×10^6, 1×10^6, and 3×10^5 cms. The capacities C_1 and C_3 were each a battery of 20 tin plates separated by glass, the capacity of which varied by about .0012 microfarad for each pair of tin plates.

2. In the previous paper[1] it was suggested that the asymptotic feet of the current-voltage curves obtained were caused by the formation of negative ions between the plates, due to the attachment of electrons to impurities present. These ions would not be removed by the high-frequency oscillations, and thus would build up a diffusion potential which would produce just such feet. In that paper the result of an attempt made to eliminate these by means of a small field of constant value which would pull the ions back to the lower plate was reported. The attempt failed in part because the fields used were too weak, and in part because of the fact that a portion of the feet were apparently due to instrumental irregularities of small magnitude in the ion chamber. In the present case two small flash-light cells giving a total potential difference of six volts were placed between the condenser C_3 and the lower plate P, so that the plate P was attached to the positive terminal of the cells. This arrangement was quite successful in eliminating the feet as may be seen in the curves of Fig. 2. In this figure the curves with crossed points represent the curves obtained without the cells, in hydrogen contaminated with about 1/3000 its volume of air. Such a contamination of the H_2 with air augmented the asymptotic feet very perceptibly. The curves

with the circled points are the mobility curves obtained under the same conditions with the cells inserted. It is seen that the curves obtained

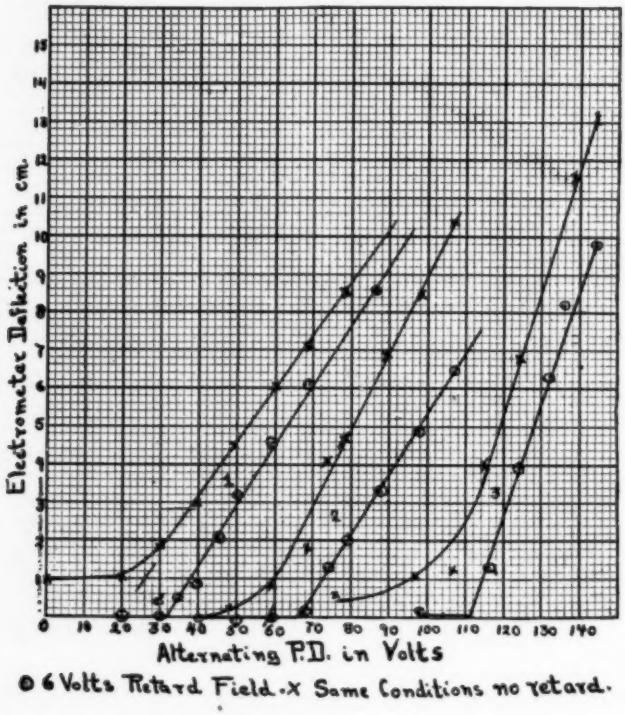


Fig. 2.

with the cells cut the axis sharply at a value close to six volts above the value obtained from the extrapolated portions of the crossed curves. This is just what was to be expected if the feet were due to ions, the effect of the retarding field being to remove the feet, and to increase the critical voltage by six volts.[1] Since the values of the mobilities obtained in the two cases are the same it is immaterial which method is used in measurement, both the cells and extrapolation giving correct values. The important point is that *these feet are not an essential attribute of electron mobility curves*, and are due to causes other than peculiarities of the electrons.

3 and 4. The improvements numbered 3 and 4 are self evident. As regards 3 it might be pointed out in passing that the inaccuracies present in the measurements of mobilities in N_2 made it impossible to detect the gradual contamination of the gas which remained in the metal chamber

[1] The latter will obviously cease to be true when the fixed potential becomes an appreciable fraction of the critical voltage. However at the critical voltages below 20 volts the asymptotic feet are generally negligible, in pure H_2, and retarding fields may be dispensed with.

more than three or four days. This contamination caused changes in the mobility of less than ten per cent., and these occurred chiefly in the case of mobilities taken with low fields where the impurities were most active. Thus the mobilities at a given pressure in N_2 seemed to be quite reproducible over several days when high fields were used, while those at low fields showed a change. With the inaccuracies due to other causes of the same magnitude superimposed on this effect it became impossible to correlate it with the ageing of the gas. In H_2 where the precision was far higher, such a change at once became evident.

The hydrogen used came from a commercial tank and was carefully purified by passing over hot copper, NaOH, $CaCl_2$, through two tubes of P_2O_{50}, and through two traps cooled with liquid air. Spectroscopic examination showed only H_2 and Hg present, though it is doubtful how delicate this test was. The procedure of measurement was precisely that followed in the case of N_2. The mobility constant K, as computed from $K = (2.2nd^2/760V_0)p$, was plotted as ordinate against the value of V_0 as abscissa as before. The points thus obtained under the best conditions are shown in Fig. 3. It is seen that in H_2 the mobility varies in much the same manner as it did in N_2. The full lines represent an attempt to fit an equation of the form $K = a/(b + V_0)$ to the points obtained for the pressures 635, 303, 151, and 73 mm. respectively. The dotted lines represent an equation of the form

$$K = \left(\frac{a}{b + V_0}\right)^{3/4}$$

applied to the same points. The equations fit the points nearly equally well, the dotted curve showing perhaps a slightly better fit. In the case of the full line curves, the curves for different pressures fall quite closely into a family of curves whose equation is

$$K = \frac{2.74 \times 10^6}{399 + \frac{V_0}{d}\left(\frac{760}{p}\right)^{3/4}}.$$

The attempt to incorporate the dotted curves for different pressures into a family of curves of the form

$$K = \left(\frac{1.09 \times 10^7}{81.3 + \frac{V_0}{d}\left(\frac{760}{p}\right)^{5/8}}\right)^{3/4}$$

was nearly as successful. Thus we must conclude that the equation

$$K = \frac{2.74 \times 10^6}{399 + \frac{V_0}{d}\left(\frac{760}{p}\right)^{3/4}}$$

seems to represent the observed results with the greatest accuracy. Here K is the mobility, p the pressure in mm., V_0 the critical voltage in volts, and d the plate distance in cm.

This equation for H_2 differs from that for N_2,

$$\left(K = \frac{5.71 \times 10^5}{21 + \frac{V_0}{d}\left(\frac{760}{p}\right)}\right),$$

in form only in that the pressure ratio $(760/p)$ in the case of H_2 is raised to the 3/4 power, while the power of $760/p$ in N_2 is 1. It seems likely that this difference is due to the uncertainty of the earlier measurements in N_2. For by applying the correction to the results in N_2 indicated by the conditions of the improved technique the curves obtained show changes which would make the factor $(760/p)$ in the present equation become $(760/p)^{3/4}$.

The theoretical equation for the mobility of electrons in a gas where they make partially elastic impacts with gas molecules as suggested by Townsend [1] is of the form

$$K = \frac{.815eL}{mc\sqrt{1 + \frac{.575V_0eL}{mc^2d\sqrt{f}}}},$$

where L is the electron mean free path, e its charge, m its mass, c its velocity of thermal agitation, and f the fraction of its energy lost at each impact. This equation demands that the mobility K should vary as

$$K = \left(\frac{a}{b + \frac{V_0}{d}\left(\frac{760}{p}\right)}\right)^{1/2},$$

where a and b are functions of L and f. As the experimental equation has the form above one may then conclude that in H_2 as in N_2 either the mean free path (L) of the electron, its loss of energy on impact f, or perhaps both of these quantities, vary as a function of the energy of the electron, *i.e.*, depend on V_0/d and $760/p$. No conclusion can at present be drawn as to which one of these factors is the more important variable,

[1] L. B. Loeb, PHYS. REV. (N. S.), 19, 1922 (24).
L. B. Loeb, Proc. Nat. Acad. Sciences, 7, 1921 (307).

though it is hoped that results obtained in He may shed light on this question. The results of Ramsauer,[1] Mayer,[2] and Townsend [3] on the variation of the electronic mean free path in argon with the electron velocity, and the results obtained by Townsend [3] on the variation of the

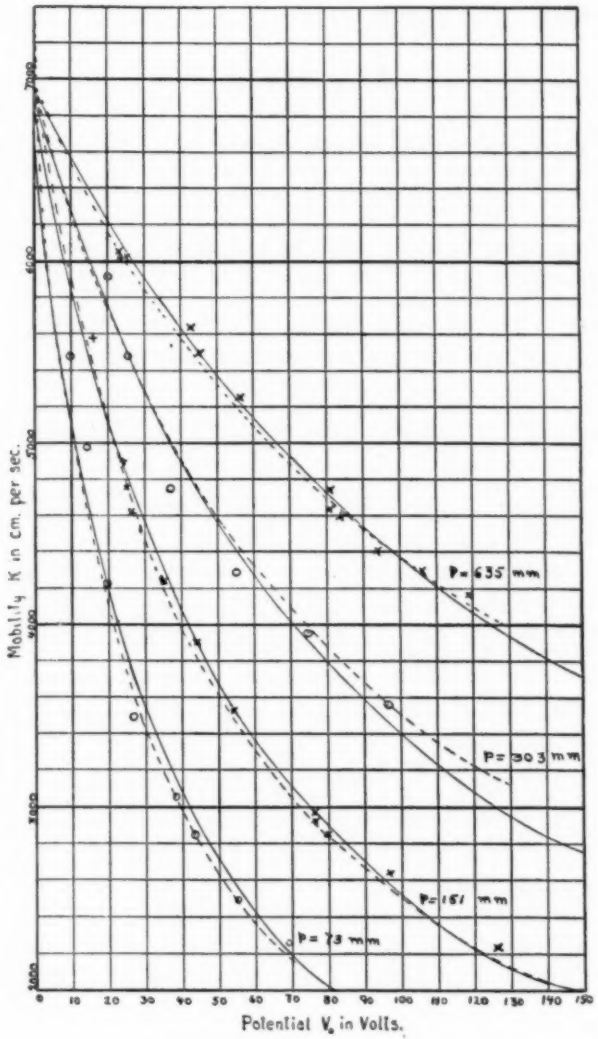


Fig. 3.

mean free paths with the electron velocity in other gases, indicate that a variation of the mean free path may possibly be the cause of the deviation of the observed mobilities from those demanded by the theory.

[1] C. Ramsauer, Ann. d. Phys., 64, 1921 (513).
[2] H. F. Mayer, Ann. d. Phys., 64, 1921 (451).
[3] J. S. Townsend and V. A. Bailey, Phil. Mag., 43, 1922 (593).

In the case where the field becomes very small (*i.e.*, for V/d approaching 0), the observed equation for the variation of K with V_0 approaches a constant value $K_0 = a/b$ which may be compared with the value of K_0 predicted by the kinetic theory. For in this case the electron absorbs no appreciable energy from the field, and its energy is that of the agitation of the molecules. The kinetic theory gives K_0 for electrons as

$$K_0 = \frac{.815e}{m}\frac{L}{c}.$$

Computing K_0 for N_2 it was found that the observed value was about 3.9 times as great as the computed value. In the case of H_2, K_0 computed is 13,060, while K_0 observed turns out to be but 6860. The observed mobility is then .53 the computed one. This difference of observed and computed values must be interpreted as meaning that the mean free paths assumed by the kinetic theory differ from those actually existing. For the mean free paths are the only factors of the equation which could vary in this case.

Thus the mean free path of electrons in N_2 is about four times that assumed by kinetic theory, a result similar to that found by Townsend, Mayer, and Ramsauer, for argon at much higher electron velocities; while the mean free path of electrons in H_2 is .53 that assumed by kinetic theory. An explanation for the low value of the mean free path found in hydrogen may be sought in the explanation given to the low values of the mobilities found for *gas ions* on the "small ion" theory. On this theory the reduction of the mobility is explained by assuming that the field of the electron acts on the surrounding gas molecules, and so by either losing momentum it has gained in the field, or by making its collisions with molecules more frequent, it effectively seems to shorten its mean free path. Why H_2 should show this latter effect while in nitrogen this effect seems to be absent furnishes a problem for the future.

NATIONAL RESEARCH FELLOWSHIP,
RYERSON PHYSICAL LABORATORY,
June 12, 1922.

THE SCATTERING OF X-RAYS BY CRYSTALS.

BY G. E. M. JAUNCEY.

SYNOPSIS.

Scattering of X-rays by Crystals (Rocksalt and Calcite), Metal (Aluminum) and Amorphous Solid (Glass).—Both homogeneous rays (K_α of Mo obtained by preliminary reflection from a rocksalt crystal) and heterogeneous rays direct from a Mo or W target (70 to 110 kv.) were used, and *scattering curves* were obtained by measuring the ionization for various angles of scattering. On account of the small intensity of the scattered radiation, incident beams of 15′ to 3° width and a scattered beam of 6° width were required even with a sensitive Compton electrometer. For angles from 50° to 150° the curves obtained for the crystals are of the same shape as those for Al and glass, each curve showing a minimum at about 100°; but for angles below 50° the crystal curves fall below the others and each shows a maximum at a larger angle, between 15° and 30°, depending on the wave-length. In addition to the general scattering at all angles, there appear, for the crystalline substances, maxima corresponding to the Laue spots. When correction for the absorption of the crystal is made, for which a formula is given, the scattering in a particular direction is found not to depend on the orientation of the crystal. This indicates that the atoms are isotropic. As was to be expected the scattered radiation was softer than the primary. For the width of x-ray beams used the total energy scattered in all directions was an appreciable fraction (0.70 for homogeneous Mo K_α rays on calcite) of the energy reflected in a first order spectrum line. *Comparison with the Debye theory* shows fair agreement only in the case of rocksalt for angles greater than 60°. For calcite there is no agreement and the prediction that the scattering by amorphous substances should be quite different from that by crystals is not verified. Applying the Thomson formula, however, the number of electrons per molecule for each crystal has been calculated from the relative amount of energy scattered at 90° and comes out of the right order of magnitude.

IN his paper on the "Interference of Roentgen Rays and Heat Motion," Debye[1] states that the regular reflection of x-rays from a crystal surface is accompanied by diffusely scattered radiation which is the most intense at those angles at which the intensity of the regularly reflected radiation is least. He finds that, if the crystal is set at such angles as to reflect a particular x-ray spectrum line in different orders, and if the ionization chamber is set to receive the reflected beam in each order, the heat motions of the atoms should cause the intensity of the different orders to fall off as the number of the order increases. On the other hand, this thermal agitation causes the intensity of the diffusely scattered radiation to increase as the angle with the primary beam of x-rays increases. In another paper,[2] Debye discusses the effect of the

[1] P. Debye, Ann. der Phys., Band 43 (1914), pp. 49–95.

[2] P. Debye, Ann. der Phys., Band 46 (1915), pp. 809–823.

regular arrangement of the electrons in the atoms upon the x-ray scattering when the atoms themselves have the random arrangement characteristic of amorphous substances. Comparing these two papers, it appears that the general scattering by crystals should be quite different from that by amorphous substances. The present experimental investigation was undertaken primarily to see if the difference predicted by Debye really occurs.

EXPERIMENTAL METHODS.

If the primary x-rays strike a crystal face at a glancing angle θ, the regularly reflected rays occur at an angle 2θ with the primary rays. In the experiments described in this paper the ionization chamber instead of being set at an angle 2θ with the primary rays is set at some other angle ϕ. The intensity of the diffuse scattering in different directions is thus measured, and curves showing the variation of the intensity of the scattered radiation with the angle are obtained. These curves are then compared with similar curves obtained using amorphous substances.

In the first experiments, x-rays from the molybdenum target of a Coolidge tube, after reflection from rocksalt to isolate the K_α line, fell upon the crystal under investigation. The second crystal was now placed at the appropriate angle θ for the regular reflection of the molybdenum K_α line in either the first or second order (see Fig. 1). Keeping the

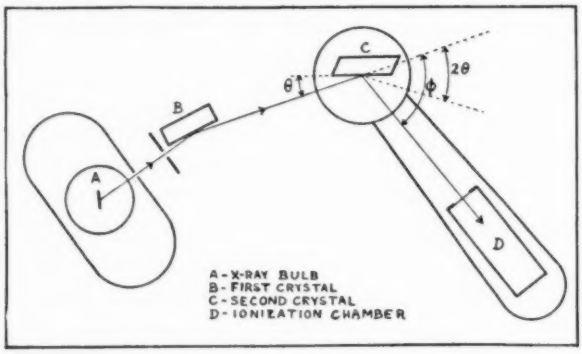


Fig. 1.

crystal in this position, readings were taken with the ionization chamber at various angles ϕ between 8° and 90°. The tube was operated by an x-ray transformer at about 70 kilovolts, and the current, 4 milliamperes, was controlled by a Victor current stabilizer. It was found that with this stabilizer it was not necessary to employ a balance method for measuring the x-rays.

The ionization chamber was filled with a mixture of methyl iodide vapor and air, and the ionization current produced in the ionization chamber measured by the deflection of a Compton electrometer operating at a sensibility of about 2500 millimeters per volt. With this two-crystal method the deflection due to the diffuse scattering of the x-rays from the second crystal was only a few millimeters per minute. As there was some difficulty in this method of eliminating small deflections due to stray scattering, a set of readings was taken with the second crystal in position and another set at the same angles with the second crystal removed. The reading with the second crystal removed was subtracted from the reading with the second crystal in position for each angle and the difference plotted against the angle of the ionization chamber. In this way the effect of stray scattering was eliminated.

In many of the experiments, especially those in which the scattering at large angles was measured, the first crystal of Fig. 1 was removed, and the x-rays fell directly upon the crystal under investigation. Though this single-crystal method employs heterogeneous x-rays, it was necessary in certain cases where the double-crystal method would have given an intensity too small for accurate measurement. With the single-crystal method, x-ray tubes with molybdenum and tungsten targets were used. In the case of the molybdenum tube the crystal, either rocksalt or calcite, was placed at an angle to reflect the molybdenum K_α line in the first order. With the tungsten tube the crystal was set to reflect only the general radiation, but was operated at different potentials, 70, 95 and 110 kilovolts.

The aluminum window of the ionization chamber which received the scattered x-rays from the crystal under investigation was 3 cm. high and 1.5 cm. wide. The distance of this window from the axis of the spectrometer was 14.3 cm., so that the angle subtended by the window at the face of the scattering crystal was 6°. Using the two-crystal method, when both crystals were set to reflect the molybdenum K_α line and the ionization chamber was placed so as to receive the regularly reflected beam from the second crystal, it was found that by rotating the second crystal through about 30′ on either side of the maximum the intensity of the reflected line fell to half value, so that the angular width of the beam incident on the second crystal can be taken at approximately 1°. With the single crystal method, beams of angular widths 3°, 45′ and 15′ were used.

EXPERIMENTAL RESULTS.

Double-Crystal Method.—The scattering curves obtained with rocksalt as the second crystal when set to reflect the molybdenum K_α line in

the first and second orders are shown as Curves *a* and *b* respectively of Fig. 2. Curve *c* is a similar curve for calcite when set to reflect the line

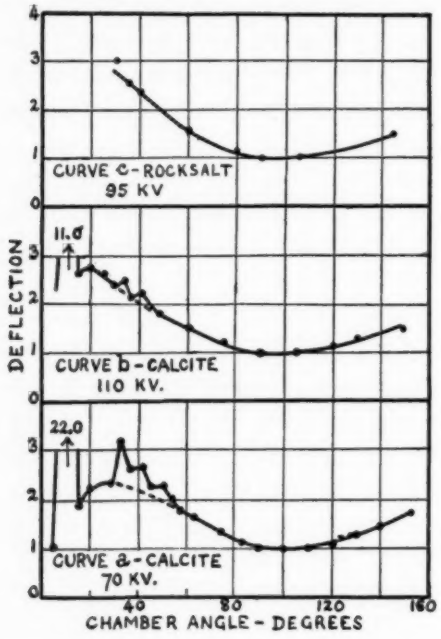


Fig. 2.

in the first order. Supplementary experiments showed that the beam incident upon the second crystal contained no appreciable x-rays of wave-length differing considerably from the K_α line. It will be noted that, even with the wide slits which were used, the intensity of the diffusely scattered radiation is only a fraction of 1 per cent. as great as the intensity of the first order reflection. In the case of calcite there is distinct evidence of a line reflected into the ionization chamber at 79°, though the crystal face is at a glancing angle of 6° 45′ with the incident beam.

It seemed possible that the intensity of the x-rays scattered by a crystal in a certain direction ϕ might be altered if the second crystal were turned out of the position in which it regularly reflected the molybdenum K_α line. It is known that the absorption coefficient of homogeneous x-rays in a crystal is increased when the rays are incident at the proper angle. Due to this increase of absorption coefficient the x-rays incident on the crystal will not penetrate so far into the crystal, and there should be less scattering. The chamber was accordingly set at an angle of 65° while the rocksalt crystal was set at various angles between 6° 20′ and 11° 20′. Fig. 3 shows the curve obtained. It will be seen that there is

no evidence of a minimum at 7° 20′, the angle at which the K_α line is reflected. The explanation of this is probably that the beam incident on the second crystal has a considerable angular width. It is only those rays which strike the crystal at the correct angle whose absorption coefficient is increased. With a wide beam such as used in these experi-

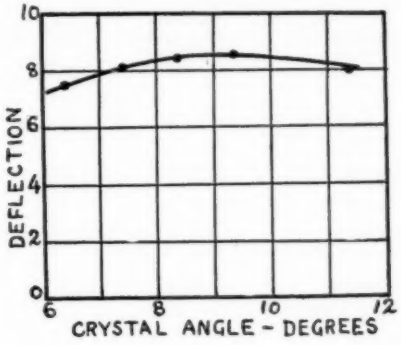


Fig. 3.

ments only a small fraction of the incident beam suffers this extra absorption.

The ratio of the intensity of the x-rays scattered at 90° to the energy of the beam of x-rays incident upon the second crystal is of considerable theoretical importance. The ratio is so small that it was necessary to obtain first the ratio of the intensity of the diffusely scattered x-rays to the energy of the regularly reflected rays when the crystal was set to reflect the molybdenum K_α line in the first order. The current through the x-ray tube was then greatly reduced, and the ratio of the deflection due to the regular reflection to that when the incident rays entered directly into the ionization chamber was obtained. The product of these ratios gives the ratio of the intensity of the x-rays scattered at 90° to the energy of the primary rays. The results are shown in the fourth column of Table I. Because of the small deflections given by the scattered x-rays these ratios are only approximate.

Single-Crystal Method.—When the direct radiation from the molybdenum tube fell upon a crystal of rocksalt, Curve *a*, Fig. 4, is obtained. In addition to the general scattering there appears a regularly reflected beam at 51°, though the crystal face makes an angle of 7° 20′ with the primary beam, the angular width of which was 45′. The corresponding curve for calcite is shown in Curve *b*, Fig. 4. In this case the angular width of the primary beam was 3°. With the calcite crystal there are regularly reflected beams at 28°, 38° and 79°. The line at 79° was previously noticed in Curve *c*, Fig. 2. These curves for rocksalt and

calcite are drawn to have equal ordinates at 90° and are typical of all the curves obtained. There is scattering at all angles, but superimposed

TABLE I.

Intensity of X-Rays Scattered at 90°.

Crystal.	Nature of X-Rays.	Linear Absorption Coefficient in Crystal.	Intensity of Scattered Rays. / Energy of Primary Rays.	Apparent Number of Electrons per Molecule.
Rocksalt.....	Homogeneous Mo-K_α Line	17.5	1.4×10^{-5}	16.3
Calcite.....	Homogeneous Mo-K_α Line	25.0	2.0×10^{-5}	47.6
Rocksalt.....	Heterogeneous Tungsten Tube	1.39	4.0×10^{-4}	29.7
Calcite.....	Heterogeneous Tungsten Tube	0.88	5.3×10^{-4}	34.2
Aluminum Sheet.....	Heterogeneous Molybdenum Tube	6.7	5.2×10^{-5}	8.5

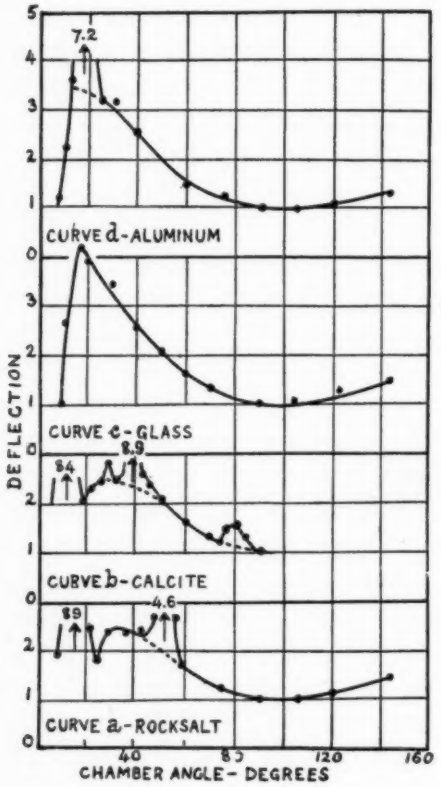


Fig. 4.

on the general scattering there is regular reflection at particular angles when the crystal is set at a certain angle.

An absorption experiment showed that the rays causing the large deflection at 38° with calcite are the molybdenum K_α rays. The humps at both 38° and 79° disappear if the orientation of the crystal is slightly changed, showing that these are undoubtedly regular reflections. There is however no such evidence of regular reflection at angles where no humps appear on the curve.

The Curves *c* and *d* of Fig. 4 were obtained when plates of glass and aluminum respectively were used in place of the crystal, the glancing angle for glass and aluminum being 8°. Otherwise these curves were obtained under the same conditions as the curves for the crystals. In addition to the general scattering, the curve for the aluminum shows evidence of regular reflection at 19°. This is due to the fact that aluminum is not amorphous but an agglomeration of minute crystals, and a powdered crystal effect is obtained.

A variation in the experiment with calcite was made by setting the chamber at an angle of 56° and turning the crystal from 5° to 56°. The curve so obtained is shown in Curve *b*, Fig. 5. Regularly reflected

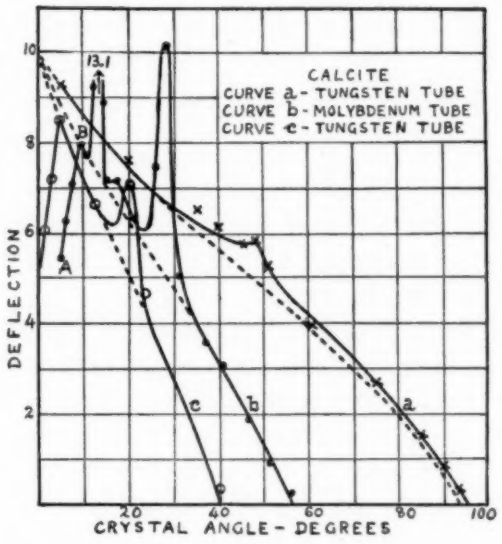


Fig. 5.

beams are obtained when the crystal is at 13° and 28°. The slope of the portion *AB* of the curve is due to the fact that at small angles of the crystal part of the primary x-rays pass by the crystal without striking it.

Using a tungsten tube, Curves *a*, *b* and *c* of Fig. 6 were obtained, the

crystal angle in each case being 5°. These curves are reduced to the same ordinate at 90°. Curve *a* is for calcite with the tube operated at a potential of 70 kilovolts, while the potential for Curve *b* was 110 kilovolts.

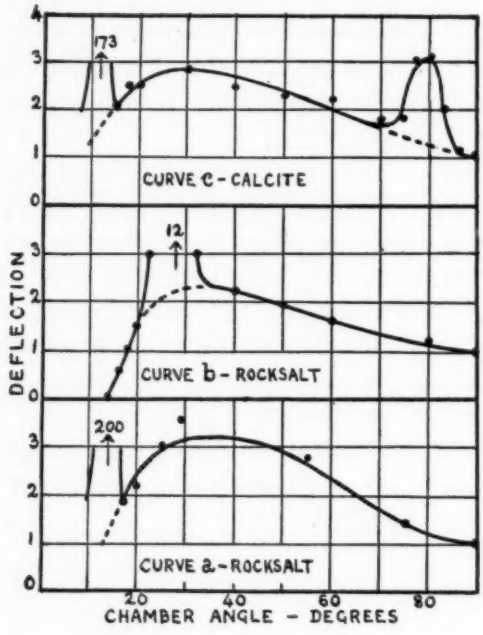


Fig. 6.

Regular reflection appears at 34° and 40° in each case, but with the greater potential the intensity of the general scattering is relatively much stronger. The angular width of the primary beam was 15′. Curves *a* and *c* of Fig. 5 were obtained by setting the chamber at 94° and 40° respectively and turning the crystal.

The quality of the radiation diffusely scattered by calcite was tested by placing an aluminum absorbing screen alternatively in the path of the primary and of the scattered beam. It was found that the scattered rays were somewhat more readily absorbed than the primary rays which produced them. This result is in accord with the scattering measurements made by others on non-crystalline substances.[1]

The ratio of the intensity of the x-rays scattered at 90° to the energy of the primary rays was measured by a method similar to that for the homogeneous x-rays. The results are shown in the fourth column of Table I. The calcite and rocksalt crystals were set at 5° while the aluminum plate was set at 8°.

[1] Cf. Sadler and Mesham, Phil. Mag., Vol. 24 (1912), pp. 138–149; A. H. Compton, Nature, Vol. 108 (1921), p. 366; et al.

DISCUSSION OF RESULTS AND CALCULATIONS.

The scattering curves show that crystals scatter x-rays in a manner similar to amorphous substances, but that in addition to this general scattering there are regularly reflected beams in certain directions with the crystal set at a given angle. Not all of these humps are due to spectrum lines, although some of them are. For instance the hump at 38° in Curve *b*, Fig. 4 was shown to be due to the molybdenum K_α line. In other cases, however, reflection is obtained from some plane in the crystal which will reflect a certain wave-length λ of the general radiation falling upon the crystal according to the equation $n\lambda = 2d \sin \theta$.

It might be supposed that the intensity scattered by a crystal molecule in a certain direction ϕ with the primary x-rays might depend upon the orientation of the molecule with respect to the primary rays. In other words, if the ionization chamber is set at an angle ϕ and the crystal turned there might be a difference in the molecular scattering in the direction ϕ as the crystal is turned. Curves for this case have been obtained in Fig. 5. Those curves are of course for the scattered radiation which gets out of the crystal. Let us suppose that the linear scattering coefficient of the crystal for a direction ϕ is s_ϕ irrespective of the orientation of the crystal relative to the primary beam. It can be shown that, if the linear absorption coefficient of the primary x-rays in the crystal is k (the slight difference between k for the primary and for the scattered rays being neglected), the intensity of the scattered x-rays leaving a thick crystal in a direction ϕ is

$$(1) \qquad \frac{s_\phi I_0}{k} \cdot \frac{\sin(\phi - \theta)}{\sin(\phi - \theta) + \sin\theta},$$

where I_0 is the energy of the primary x-rays and θ is the glancing angle of the primary rays upon the crystal face. If ϕ is kept constant, formula (1) may be written in the form

$$(2) \qquad \text{constant} \times \frac{\sin(\phi - \theta)}{\sin(\phi - \theta) + \sin\theta}.$$

The broken curves in Fig. 5 are obtained by plotting values of (2) against θ for $\phi = 90°$, 56° and 40° respectively, the appropriate value of the constant being taken in each case. It is seen that the experimental curves correspond with the theoretical curves excepting for the humps due to regular reflection. The result implies that the intensity of the rays scattered by a crystal molecule in a given direction ϕ does not depend upon the orientation of the crystal, and that therefore the atoms of the crystal are nearly isotropic.

The scattering curves should be corrected for absorption in the crystal in order to give the true molecular scattering in various directions. If each of the ordinates of each of the experimental scattering curves is divided by formula (2), the true scattering curves shown in Fig. 7 are

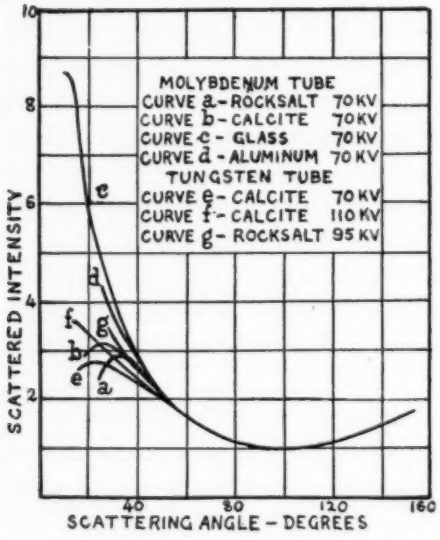


Fig. 7.

obtained, the humps due to regular reflection being omitted. These curves are drawn so as to have the same ordinate at 90°. Curves *a*, *b*, *c* and *d* are for heterogeneous x-rays from a molybdenum tube, while Curves *e*, *f* and *g* are for heterogeneous x-rays from a tungsten tube. It is seen that the curves are practically identical for the range $\phi = 50°$ to $\phi = 150°$. In this range the crystal curves (*a*, *b*, *e*, *f* and *g*) coincide with the curves for aluminum and glass (*c* and *d*). Below 50° the crystal curves all fall below the aluminum and glass curves. The crystal curves all reach a maximum between 15° and 30°. The curves for calcite and rocksalt, when the primary rays are homogeneous molybdenum K_α rays, are not shown but have the same general characteristics as the curves shown. Curves *e* and *f* are for the same calcite crystal and for the same tungsten tube, the only difference being that the potential for Curve *e* is 70 kilovolts while that for Curve *f* is 110 kilovolts. It appears as though the maximum is shifted to the smaller angles for the shorter wave-lengths.

It would be interesting to examine the shape of the scattering curves for small angles. It is known that the scattering curves for amorphous substances slope down towards zero for small angles, but the maximum occurs at much smaller angles than do the maxima for crystals in the

present experiments. For instance Curve *c* which is for glass does not show a maximum above 11° whereas calcite Curve *b* shows a maximum at 25° even though both curves are for a molybdenum tube operated at a potential of 70 kilovolts. The experimental difficulties when working at small angles necessitate the abandonment of this inquiry at this time.

According to Debye[1] the intensity of the x-rays scattered in a direction ϕ from a crystal should be equal to that from an amorphous substance multiplied by $(1 - e^{-M})$, where

$$M = \frac{0.569 \times 10^{-12}}{A\Theta\lambda^2} \times (1 - \cos\phi) \times \frac{F(z)}{z}$$

when there is no zero-point energy and

$$M = \frac{0.569 \times 10^{-12}}{A\Theta\lambda^2} \times (1 - \cos\phi) \times \left[\frac{F(z)}{z} + \frac{1}{4}\right]$$

when there is a zero-point energy. In these z is the ratio of the characteristic temperature Θ of the crystal to its experimental temperature, A its atomic weight, λ the wave-length of the incident homogeneous x-rays, and $F(z)$ is a function of z which Debye evaluates. The value of the factor $(1 - e^{-M})$ has been found for both clacite and rocksalt when the incident wave-length is 0.717 Å. U., which is the wave-length of the molybdenum K_α line,[2] and the room temperature is 290° K. A. H. Compton[3] gives the characteristic temperatures of calcite and rocksalt as 910° K. and 260° K. respectively. The atomic weight of calcite is taken as the average atomic weight, viz., 20. The value of $(1 - e^{-M})$ for a certain value of ϕ is divided by the value for $\phi = 90°$. The curve obtained is shown as Curve *a*, Fig. 8. There are two possible

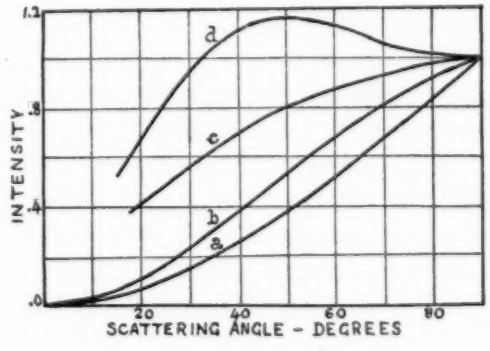


Fig. 8.

[1] Loc. cit.

[2] Kaye and Laby, Physical and Chemical Constants, 4th Ed., p. 99.

[3] A. H. Compton, PHYS. REV., Second Series, Vol. 9 (1917), p. 47.

curves, one for the case where there is no zero-point energy and the other for the case where there is a zero-point energy. The two curves, however, are very close together and the mean curve is the one shown. If each ordinate of Curve *c*, Fig. 7, which is for glass, is multiplied by the corresponding ordinate of Curve *a*, Fig. 8, the theoretical scattering curve for a crystal of calcite is obtained. This is shown as Curve *c*, Fig. 8. Curves *b* and *d*, Fig. 8, are the curves for rocksalt, the average atomic weight of rocksalt being taken as 29. It will be seen that Curve *d* which is the theoretical scattering curve for rocksalt coincides fairly well with the experimental curve for the range 90° to 60°, but below 60° there is a great discrepancy between the theoretical and experimental curves. In the case of calcite the curves do not coincide at any place.

According to J. J. Thomson[1] the intensity of x-rays falling on 1 cm.^{2} at a distance R from the scattering substance is

$$\frac{Ne^4}{R^2m^2c^4} \cdot \frac{1 + \cos^2 \phi}{2} \cdot pI_0, \tag{4}$$

where p is the number of electrons per atom (or molecule), N is the number of atoms (or molecules) per unit volume and I_0 is the energy of the primary rays. This is also the formula obtained by Debye[2] for the case of an amorphous scattering substance when the wave-length of the x-rays is small compared with the radius of the atomic electron ring. If it is assumed that the absorption coefficient of the scattered x-rays is equal to that of the primary x-rays, then the total intensity of the rays entering the ionization chamber from a thick crystal when the crystal angle is θ and the chamber angle is 90° can be shown to be

$$I_{90} = \frac{SNe^4}{R^2m^2c^4} \frac{p}{2k(1 + \tan \theta)} I_0, \tag{5}$$

where S is the area of the window of the ionization chamber and k is the linear absorption coefficient of the x-rays in the crystal. Knowing the experimental value of I_{90}/I_0 and the value of k, p the number of electrons in the atom (or molecule) of the scattering crystal can be found. The linear absorption coefficients of molybdenum K_α rays in rocksalt and calcite were not found directly but were calculated from the known coefficient for aluminum using the law that the atomic absorption of an element varies as the fourth power of the atomic number of the element. The absorption coefficients for heterogeneous x-rays were measured directly. There is considerable doubt of the coefficients

[1] J. J. Thomson, Conduction of Electricity through Gases, 2d Ed., p. 325.

[2] Loc. cit.

for heterogeneous rays as they depend upon the thickness of crystal used. It is seen that the numbers of electrons per molecule are of the right order of magnitude, the true values for rocksalt and calcite being 28 and 50 respectively. According to Debye's theory of crystal scattering the factor $(1 - e^{-M})$ should enter into the intensity scattered. The absolute value of the factor for scattering at 90° from calcite for a wave-length of 0.717 Å. U. (molybdenum K_α line) is 0.092 for no zero-point energy and 0.227 for zero-point energy, that is, the intensity scattered at 90° by a crystal of calcite should be either about one tenth or one fifth of that scattered by an amorphous substance of equal molecular weight. The fact that p comes out of the right order of magnitude and not one tenth or one fifth of the correct value shows that Debye's theory falls far short of explaining the experimental facts for calcite. For rocksalt the value of $(1 - e^{-M})$ for scattering at 90° and for a wave-length 0.717 Å. U. is 0.73 for no zero-point energy and 0.82 for zero-point energy, the two experimental values for rocksalt being 0.56 and 1.06. Hence in the case of rocksalt the theory as far as the scattering at 90° is concerned is not opposed to the facts.

The discrepancy between Debye's theory of scattering and the observed results in the case of rocksalt is remarkable because in another direction Debye's theory has received confirmation. According to Debye the energy of a regularly reflected line should be proportional amongst other things to e^{-M}. This was tested by W. H. Bragg[1] in an experiment where he heated a crystal of rocksalt and observed the energy of the rhodium line as reflected by the crystal (1) when the crystal was at a temperature of 288° K., and (2) when the crystal was at 643° K. The observed ratio of the energies was equal to the ratio as calculated from the theory. This might not have been so remarkable if the glancing angle in Bragg's experiment had been above 30°, making the chamber angle above 60°, as it is between 60° and 90° in my experiments that the scattering curve of rocksalt as found experimentally agrees to some extent with that indicated by the theory. However Bragg's experiments were done at glancing angles between 12° and 13° 30′ in the case of second order reflection and between 18° 30′ and 20° in the case of the third order reflection. In the former case the chamber angle is between 24° and 27° while in the latter case the chamber angle is between 37° and 40°. This is just the range where there is very great discrepancy between Debye's theory as applied to scattering from crystals and the experimental results of this present paper. For this reason it is a matter of great interest to test the temperature effect on the intensity of x-rays scattered by a crystal. This investigation however will be left for another paper.

[1] W. H. Bragg, Phil. Mag., Vol. 27 (1914), pp. 881–899.

From the true scattering curves of Fig. 7 it is possible to calculate the ratio between the energy of the regularly reflected beam at $\phi = 2\theta$ to the total energy scattered. The energy scattered between the two cones of semi-angles $\phi - (\delta\phi/2)$ and $\phi + (\delta\phi/2)$ is given by

$$\frac{2\pi R^2 \sin\phi\,\delta\phi}{S} \cdot y, \tag{3}$$

where y is the ordinate of one of the curves in Fig. 7 for a particular value of ϕ, R is the distance of the window of the ionization chamber from the crystal, and S is the area of the window, and $\delta\phi$ is 6°. Values of (3) are calculated for each interval of 6° and these added for the range $\phi = \phi_1$, and $\phi = \phi_2$, thus giving the total intensity of true scattering between the two cones whose semi-angles are ϕ_1 and ϕ_2. The results for calcite are shown in Table II. The ratio is calculated for homogeneous x-rays on the assumptions that the absorption coefficient in the crystal is the same when the crystal is in a reflecting position as when it is thrown out of this position, and also that the absorption coefficient of the scattered x-rays is equal to that of the primary x-rays. The ratio is therefore only an approximation. When the ratio is calculated for heterogeneous radiation consisting of the molybdenum K_α line plus general radiation a difficulty arises in that the absorption coefficient of the regularly reflected line is quite different from that of the scattered radiation. In the case of the x-rays coming from a tube with a molybdenum target the mass absorption coefficient of the general scattered radiation was 1.51 while that of the molybdenum K_α line was 5.17. A different value of k in formula (1) must be used for the line from that for the general scattered radiation.

TABLE II.

Proportion of X-Rays Regularly Reflected.

Nature of X-Rays.	ϕ_1.	ϕ_2.	Energy of Regularly Reflected X-Rays. / Energy of Scattered Radiation
Homogeneous Mo K_α line.....	14°	93°	2.85
Heterogeneous Mo K_α line plus General Radiation.....	15°	153°	0.66

Calcite Crystal Set for First Order Reflection of Mo K_α Line.

There is also scattering of the homogeneous x-rays in the ranges 0° to 14° and 93° to 180°. The scattering throughout the whole range 0° to 180° is about double of that in the range 14° to 93°. The energy of the regularly reflected line is therefore about 1.43 times that of the total scattering. This is for the case where the angular width of the

primary beam is about 1°. For heterogeneous x-rays the proportion reflected is much less, being 0.66 of the amount scattered in the range 15° to 153°. Taking the whole range 0° to 180°, the energy reflected in the line is about one half of the total energy scattered. This is for an angular width of the primary beam equal to 45′. For higher orders of reflection these ratios are much smaller and are smaller still for the case where the crystal is not set to reflect a line but general radiation. The total energy scattered from a crystal is less than that scattered from glass. Comparing calcite and glass using a molybdenum tube and interpolating Curves *b* and *c* of Fig. 7 for the angles 0° to 15°, the ratio of the total energy scattered by the crystal to that scattered by the glass for the range 0° to 150° is 0.85. It was thought that the regular reflection from a crystal might take place at the expense of the general scattering and that the difference between the energy scattered by glass and by a crystal might be equal to the energy of the regularly reflected radiation. This however is not the case.

Summary.

The scattering of x-rays by the crystals calcite and rocksalt has been examined and the following results found:

1. The scattering curves for rocksalt and calcite are of the same shape as the curves for the amorphous substances glass and aluminum for the range 50° to 150° with the direction of the primary rays. The minimum of all the curves occurs at about 100°.

2. For scattering angles below 50° the crystal curves fall below those for the amorphous substances. The crystal curves reach a maximum between 15° and 30°, the position of the maximum being at smaller angles for smaller wave-lengths. The maximum in the case of amorphous substances occurs at much smaller angles than in the case of the crystals.

3. From the ratio of the intensity of the x-rays scattered at 90° to the energy of the primary rays the number of electrons per molecule of each crystal has been calculated by means of Thomson's formula. The numbers as calculated are of the right order of magnitude.

4. The x-rays scattered from crystals are softer than the primary x-rays, in this way resembling the x-rays scattered from amorphous substances.

5. A comparison between the experimental results and the theory of crystal scattering as developed by Debye has been made. It is shown that Debye's theory falls far short of explaining the observed facts. In the case of rocksalt there is fair agreement between the intensity scattered at 90° and that predicted by Debye, but at angles below 60° the difference between theory and experiment becomes great. For

calcite there is no agreement whatever between theory and experiment. This may be due to the fact that $CaCO_3$ is a more complicated molecule than NaCl.

6. In addition to the general scattering at all angles from a crystal, there appear Laue spots at particular angles.

7. The energy of x-rays scattered by a crystal in all directions is an appreciable fraction of the energy of a regularly reflected line.

8. The intensity of x-rays scattered in a certain direction is independent of the orientation of the crystal which suggests that the atoms are nearly isotropic.

9. The total scattering was not appreciably changed by turning the crystal from a position where a spectrum line was regularly reflected to a position where the line was not reflected.

In conclusion the author wishes to express his thanks to Professor A. H. Compton for his interest and aid in the preparation of this paper.

WASHINGTON UNIVERSITY,
ST. LOUIS, MO.,
June 8, 1922.

THE EFFECT OF TEMPERATURE ON THE SCATTERING OF X-RAYS BY CRYSTALS.

BY G. E. M. JAUNCEY.

SYNOPSIS.

Variation of the Scattering of X-Rays by Rocksalt and Calcite with Temperature.—Using x-rays from the *W* target of a Coolidge tube operated at 95 kv., the ratio of the radiation scattered from a crystal at 295° C. to that scattered at the same angle from the crystal at 17° C. was found to be: 1.33 and 1.18 ± .10 for rocksalt and angles of 15° and 30° respectively, and 0.99 and 1.03 ± .04 for calcite and angles of 30° and 73° respectively. Thus there is a marked effect for rocksalt but apparently none for calcite, which seems to scatter x-rays like an amorphous substance. *Comparison with the Debye theory* shows that even for rocksalt the effect is considerably smaller than that theoretically predicted, whether zero-point energy is assumed or not, while for calcite the disagreement is marked.

DEBYE [1] has developed a theory of the scattering of x-rays in which he predicts that the intensity of the x-rays scattered in a direction ϕ with the primary rays should be proportional to $(1 - e^{-M})$, where

$$M = \frac{0.569 \times 10^{-12}}{A\Theta\lambda^2} \times (1 - \cos\phi) \times \frac{F(z)}{z}$$

for no zero-point energy, and

$$M = \frac{0.569 \times 10^{-12}}{A\Theta\lambda^2} \times (1 - \cos\phi) \times \left[\frac{F(z)}{z} + \frac{1}{4}\right]$$

for zero-point energy. In these expressions, λ is the wave-length of the x-rays, A the atomic weight, Θ the characteristic temperature of the crystal, z the ratio of the characteristic temperature of the crystal to its experimental temperature, and $F(z)$ is a function which Debye evaluates. As shown by the author in a previous paper,[2] Debye's theory falls far short of explaining the scattering curves for the crystals calcite and rocksalt obtained experimentally and it is therefore of interest to determine how the temperature affects the intensity of the x-rays scattered in a certain direction ϕ.

The crystal to be investigated was placed with its (100) face on the axis of a Bragg spectrometer as in the single crystal method described in the previous paper. In the present experiment, however, the crystal

[1] P. Debye, Ann. der Phys., Band 43 (1914), pp. 47–95.

[2] G. E. M. Jauncey elsewhere in this issue of the PHYS. REV.

was surrounded by a heating box, supplied with mica windows. The x-rays from a Coolidge tube with a tungsten target, which was operated at a potential of 95 kilovolts in most cases and at a potential of 70 kilovolts in one case, passed through the mica windows. The crystal face was set at an angle θ, and the ionization chamber at an angle ϕ, with the primary rays, care being taken that only diffusely scattered rays and no regularly reflected rays entered the chamber. A set of 10 readings was taken at the room temperature, which was 290° K., a second set was taken at a temperature of 568° K., and a third set when the crystal had cooled to room temperature again. The average of the second set was divided by the average of the first and third sets. The results are shown in the third column of Table I. The temperature was measured with a mercury-in-glass thermometer. In order to be sure that the crystal was at the temperature of the thermometer, the readings at the high temperature were not taken until one hour after the thermometer first registered 568° K. The change of the sensitivity of the electrometer during this time was measured and allowed for.

TABLE I.

$$\frac{\text{Scattered Intensity at 568° K.}}{\text{Scattered Intensity at 290° K.}}$$

Crystal	Scattering Angle.	Experimental Value.	Theoretical Value.	
			No Zero-Point Energy.	Zero-Point Energy.
Rocksalt [1]	15°	1.33	1.87	1.65
Rocksalt [1]	30°	1.18	1.37	1.26
Calcite[1]	30°	0.99	2.64	1.56
Calcite[1]	73°	1.03	2.03	1.25
Calcite[2]	73°	1.03	2.23	1.29

The theoretical values are calculated from Debye's formula. These are shown in the fourth and fifth columns of Table I. The mass absorption coefficient of the x-rays in aluminum was measured, the mean of the coefficients when the aluminum was placed in the primary and when it was placed in the scattered beam being taken. From the relation between the absorption coefficient and the wave-length given by Hewlett,[3] the effective wave-length of the scattered x-rays was found. The average atomic weight of $CaCO_3$ was taken as 20 and that of NaCl as 29. The characteristic temperatures of calcite and rocksalt[4] are 910° K. and 260° K.

[1] Wave-length 0.28 Å. U

[2] Wave-length 0.36 Å. U.

[3] C. W. Hewlett, PHYS. REV., Second Series, Vol. 17 (1921), pp. 284–301.

[4] A. H. Compton, PHYS. REV., Second Series, Vol. 9 (1917), p. 47.

It will be seen that rocksalt shows a temperature effect, but not so large as that predicted by Debye on the assumption of either no zero-point energy or zero-point energy. Calcite on the other hand shows practically no temperature effect. The ratios in the third column are correct to 8 per cent. in the case of rocksalt and to 4 per cent. in the case of calcite. It might be argued that one is not justified in taking 20 as the average atomic weight of calcite as the atomic weights vary from 12 to 40. The ratio for zero-point energy for a wave-length of 0.28 Å. U. and scattering angle 73° has been calculated to be 1.12 for an atomic weight of 12 and 1.45 for an atomic weight of 40. The experimental value is still much less than the smaller of these two values.

These results are in accord with the results of the previous paper. There is a very rough agreement between Debye's theory, assuming a zero-point energy, and the experimental results for rocksalt, but there is no agreement for calcite. Calcite seems to act very similarly to an amorphous substance as far as scattering is concerned. This seems to indicate that the electrons in the calcite molecule which cause the scattering act more or less independently of one another.

In a recent theoretical paper by Brillouin,[1] doubt is thrown upon the validity of the theory of Debye. Brillouin intimates that the scattering from crystals may be unaffected by the temperature.

WASHINGTON UNIVERSITY,
ST. LOUIS, MO.,
June 8, 1922.

[1] L. Brillouin, Ann. de Phys., Tome 17 (1922), pp. 88–122.

THE CRYSTAL STRUCTURE OF SILVER–PALLADIUM AND SILVER–GOLD ALLOYS.

BY L. W. MCKEEHAN.

SYNOPSIS.

Crystal Structure of Silver, Gold and Palladium and of Ag-Au and Ag-Pd Alloys.—Thin ribbons of the pure metals and of seven binary alloys of each series were prepared by fusing into small ingots and then swaging, drawing and rolling to thicknesses of from 1/400 to 1/200 cm. The x-ray diffraction patterns were photographed by allowing the K-radiation of Mo to fall for 8 to 20 hours on each ribbon. It was found that all these metals and alloys have their atoms arranged in face-centered cubic lattices. The parameter a of each lattice, the edge of the cube, has the values 4.08×10^{-8}, 4.075×10^{-8} and 3.90×10^{-8} cm. for pure Ag, Au and Pd respectively. For the Ag-Pd series, the parameter is nearly a linear function of the atomic per cent. of either component and this is also true for the Ag-Au series except that for the alloys with 30, 40 and 60 per cent. Ag the values of a came out one per cent. too high. These results are for the most homogeneous and isotropic condition and are believed to be correct to within about 1/3 per cent. *The effect of annealing* at from 830 to 940° C. for an hour or more in vacuo was to increase the size of individual crystals, to render them more homogeneous and to make their orientations more isotropic. *The effect of moderate cold working*, rolling, pressing or hammering is to reduce the size of the individual crystals and to make them less isotropic.

Densities of crystals of silver, gold and palladium, computed from the above results of X-ray crystal analysis and the atomic weights, come out 10.49, 19.24 and 11.87 respectively. The Ag and Au were pure and the Pd contained only 0.5 per cent. impurity.

INTRODUCTION.

A STUDY of the arrangement of atoms in alloys which are solid solutions of the components may throw some light on the cause of the abnormally high resistivity of such alloys. This report covers somewhat completely the crystal structure in two series of alloys, those of silver with gold and palladium, which are particularly interesting in this connection because silver and gold both possess high conductivity, whereas the conductivity of palladium is much lower than that of silver. The conductivity of the alloys is not, however, treated in this report.

PREPARATION OF ALLOYS.

The component metals were all purchased from Baker and Company, and were of high purity, the silver and gold containing less than 0.01 per cent. of impurities, the palladium containing about 2 per cent. of impurities, chiefly copper and noble metals. The chemical and metallurgical processes outlined below were conducted by Mr. J. E. Harris

and Mr. H. T. Reeve, both of this laboratory, who have had extensive experience in the preparation of alloys of known composition and exceptional homogeneity. All three metals were repurified chemically and obtained in finely divided form, the principal effect of these processes upon their purity being that the palladium finally contained less than 0.5 per cent. of impurities, copper, in particular, being completely removed. The metal powders were weighed, mixed, and pressed into small cylindrical rods of the desired compositions. The Ag-Au alloys were fused in an electrically heated furnace open to the air; the Ag-Pd alloys were fused on alundum or magnesia by the oxyhydrogen flame. The ingots, which weighed about 10 grams each, were swaged and drawn into wires about one millimeter in diameter. Short pieces of these wires were rolled to a thickness of from 0.0025 to 0.0050 cm., the rolling being carried farthest for alloys containing large proportions of gold, and hence having the highest absorption coefficients for x-rays. The condition resulting from these operations is indicated below by the letter *R*.

The annealing process consisted in maintaining the temperature of the sample at from 830° C. to 940° C. for an hour or more, in vacuo, in a quartz tube furnace, electrically heated. When several alloys were annealed at one time the samples were placed in individual quartz tubes, open at one end, to prevent mutual contamination. Temperatures were read by a calibrated platinum-platinum-rhodium thermocouple. The Ag-Au alloys required much longer annealing at these temperatures than did the Ag-Pd alloys, before the results indicated even fair homogeneity and isotropy. The longest time of annealing actually used was about 13 hours. The annealed condition is indicated by the letters *RA*.

In order to determine whether certain high values of a for condition *R* were due to distortion of the space-lattice by cold-working or to some other cause, the Ag-Pd alloys in condition *A*, were rerolled after the x-ray examination so as to reduce the thickness by from 30 to 50 per cent. The increase in stiffness caused by this second rolling was very noticeable. The condition is indicated by the letters *RAR*. Finally, after examination in condition *RAR*, these same strips were reannealed and again examined. This final condition is indicated by the letters *RARA*.

METHOD OF X-RAY ANALYSIS.

The apparatus used has been fully described by Davey,[1] and only a brief statement to define the experimental conditions will here be given. The K-radiation of molybdenum, sufficiently isolated for photographic purposes by ZrO_2 filters, is allowed to fall, for from 8 to 20 hours on the

[1] W. P. Davey, Opt. Soc. of Am. Jl., *5*, 479–493 (Nov., 1921).

face of a thin ribbon of the metal to be analyzed. The shadow cast by the edge of the ribbon, and the diffracted beams due to its suitably oriented crystals are caught by a strip of photographic film wrapped on a cylinder, the axis of which coincides with the edge of the ribbon. The current through the x-ray tube is about 30 milliamperes, the potential across it about 30,000 volts. The radius of the film (sensitive side) is $r = 20.36$ cm. for the particular film-holders here used.

The diffracted beams due to the individual crystals form full-sized images of the source,[1] which are separately distinguishable if the crystals are large enough, and which, when distinguishable, are more clearly defined the more homogeneous is the arrangement of atoms in the individual crystals. By keeping the sample at rest we thus gain information as to the dimensions of the crystals and their homogeneity. It should be mentioned that if the crystals are very large the images of the source are characteristically blurred at certain points, but this aperture effect is easily distinguishable from the general blurring of the spots due to imperfections in a smaller crystal. If the spots are numerous and intense, as in the present series of photographs, the more remote edges of the bands which they form on the photographic film are easily located within a couple of tenths of a millimeter, whether the individual spots are distinguishable or not.[2] The relative intensities of the bands will differ from the normal if the crystals are not oriented isotropically.[3] The distance from the edge of the shadow of the ribbon to the corresponding (more remote) edge of any band is $s = 2r\theta$, where θ is the grazing angle of incidence at which "reflection" takes place. The data, then, are the values of s, which range in these photographs from 6 to 30 cm. From these data the corresponding values of the perpendicular distance, d, between consecutive planes can be directly computed by the formula

$$d = \frac{\lambda}{2} \csc\left(\frac{s}{2r}\right),$$

where λ is the wave-length of the x-rays. In order to reduce the labor of computation by this formula a table was constructed giving $\log_{10} d$ to four decimals for the argument s at every 0.01 cm. from 2.50 cm. to 30.00 cm. The value of λ_2 for the longer wave-length component of the $K\alpha$ doublet, 0.71212×10^{-8} cm., used in the construction of this table, was that given by Duane and Patterson.[4] The same table was used for the

[1] L. W. McKeehan, Frank. Inst. Jl., *194* (1922).

[2] L. W. McKeehan, Frank. Inst. Jl., *193*, 231–242 (Feb., 1922).

[3] M. Polanyi, Zs. f. Phys., *7*, 149–180 (Nov., 1921).

[4] W. Duane, Nat. Res. Counc. Bull., *1*, 383–408 (Nov., 1920): W. Duane and R. A. Patterson, Nat. Acad. Sci. Proc., *8*, 95–90 (May 15, 1922).

shorter wave-length component of the doublet, $\lambda_1 = 0.70783 \times 10^{-8}$ cm., when the doublet was resolved in the photographs, by subtracting a constant correction (0.0026) from the tabulated values of $\log_{10} d$.

The values of $\log_{10} d$ were computed in this way for every measured value of s. The indices of the corresponding planes (hkl) of the space-lattice were determined by inspection, the order and spacing of the bands being characteristic of the face-centered cubic space-lattice always found for the alloys here studied. The order of reflection is conveniently included in the indices h, k, l; *e.g.*, the second order from the planes (210) is indicated by the symbol (420). An auxiliary table was computed which gives $\log_{10} a/d$ for the first 54 bands of a simple cubic space-lattice, 22 of which, having h, k, l all even or all odd, are also found in the pattern for a face-centered cubic space-lattice. With this notation the usual formula[1] becomes

$$\frac{a}{d} = \sqrt{h^2 + k^2 + l^2}.$$

Adding the corresponding tabular numbers gives $\log_{10} a$ which should be the same for all the bands. Table I. shows how nearly this condition is satisfied. The mean value of $\log_{10} a$ was taken without weighting the separate values, since the more remote bands, on account of their relative faintness, have larger absolute errors in s and yield only slightly better values of a than do the more intense bands nearer the shadow of the specimen. The first band of the pattern, which is very intense, was sometimes rejected, however, if the values of s were inaccurate on account of a poorly defined shadow. A poorly defined shadow may be due either to use of too thin a sample or to over-exposure and partial reversal of the unshaded area.

ACCURACY.

An example of the data and calculations from a single film is given in Table I., which is self-explanatory. From calculations of this kind it is apparent that the probable error in the value of a from a single experiment is low; it is estimated at about 1 part in 500. Examination of different samples presumably alike showed however that these may differ in the value of a by as much as one per cent., although generally agreeing much closer. The widest variations occurred in condition R. Such variation is not surprising, since the value of a is really determined for a sample of metal which originally occupied only about one cubic millimeter in the ingot. In conditions RA and $RARA$ it is thought that the agreement of results for different samples justifies the statement

[1] A. W. Hull, PHYS. REV., (2), *10*, 661–696 (Dec., 1917).

that a is known to 1 part in 300. The compositions of the alloys, as given in Table I., are subject to errors which it is difficult to estimate.

TABLE I.

Material: Ag_2Pd_3			Condition: RA		Film No. 298
Relative Intensity.	Arc Length, s, in cm.	Due to $K\alpha_1$ or $K\alpha_2$.	log ($d \times 10^8$).	Miller Indices.	log ($a \times 10^8$).
10.....	6.35	2	0.3603	111	0.5989
4.....	7.34	2	0.2979	200	0.5989
6.....	10.42	2	0.1482	220	0.5997
4.....	12.28	2	0.0787	311	0.5994
4.....	12.82	2	0.0606	222	0.6002
1.....	14.86	1	9.9963	400	0.5984
4.....	16.28	1	9.9586	331	0.5980
1.....	16.34	2	9.9597	331	0.5991
3.....	16.72	1	9.9477	420	0.5982
1.....	16.79	2	9.9486	420	0.5991
3.....	18.42	1	9.9083	422	0.5984
1.....	18.53	2	9.9085	422	0.5986
3.....	19.64	1	9.8825	(333 511)	0.5982
1.....	19.75	2	9.8828	(333 511)	0.5985
1.....	21.52	1	9.8462	440	0.5988
3.....	22.65	1	9.8262	531	0.5982
1.....	22.78	2	9.8266	531	0.5986
2.....	22.99	1	9.8205	(442 600)	0.5987
1.....	23.13	2	9.8207	(442 600)	0.5989
1.....	24.41	1	9.7974	620	0.5984
1.....	24.56	2	9.7977	620	0.5987
1.....	25.45	1	9.7816	533	0.5983
1.....	25.78	1	9.7768	622	0.5985

Mean value log ($a \times 10^8$) = 0.59873,
$a = 3.969 \times 10^{-8}$ cm.

Even in the silver-palladium series an error as great as two or three per cent., which is improbably high, would not affect the conclusions drawn from the results. Evidence is given below for the belief that the composition was not appreciably altered by annealing.

NUMERICAL RESULTS.

Table II. contains the values of a determined from the photographs, together with the densities computed for the most homogeneous condition examined. The values of a as a function of the atomic per cent. of silver

TABLE II.

Formula.	Atomic % Ag.	Values of $a \times 10^8$.				Computed Density.	
		R.	*RA.*	*RAR.*	*RARA.*	*RA.*	*RARA.*
Ag.....	100	4.080[1]	4.080[1]			10.49	
Ag_4Au...	80	4.104	4.081[2]			11.93	
Ag_3Au_2..	60	4.112	4.126[2]			13.50	
AgAu ...	50	4.082	4.088[2]			14.74	
Ag_2Au_3..	40	4.091	4.114			15.31	
Ag_3Au_7..	30	4.072	4.122[2]			16.06	
$AgAu_4$...	20	4.082	4.079[2]			17.44	
$AgAu_9$...	10	4.096	4.084[2]			18.24	
Au.....	0	4.075	4.075[1]			19.24	
Ag.....	100	4.080[1]	4.080[1]			10.49	
Ag_9Pd...	90	4.090	4.056	4.053	4.055		10.67
Ag_3Pd...	75	4.075	4.037	4.014	4.020		10.93
Ag_3Pd_2..	60	4.023	4.001	3.992	4.004		11.08
AgPd ...	50	4.006	3.982	3.974	3.975		11.28
Ag_2Pd_3..	40	4.004	3.969	3.949	3.956		11.43
$AgPd_3$...	25	3.949	3.945	3.952	3.934		11.60
$AgPd_9$...	10	3.924	3.921	3.930	3.909		11.81
Pd.....	0	3.900[1]	3.900[1]			11.87	

are also presented graphically in Fig. 1, for the conditions used in the computation of densities. In determining the mass to be ascribed to each unit of structure the value $N = 6.0594 \times 10^{23}$, as given by Birge,[3] and the 1921 atomic weights: Ag, 107.88; Au, 197.2; Pd, 106.7, were chosen. The densities for the pure metals: Ag, 10.49; Au, 19.24; Pd, 11.87, are within the range of values usually obtained, those for gold and silver being very close to the accepted values. The density of palladium has been a matter of some doubt, values from 11.40 to 12.16 having been reported. It is thought that the value given here is the most accurate yet obtained.

The previously published values for the space-lattice parameters of these three metals are due to Vegard [4, 5] and Hull.[6] Vegard's data has been recomputed using $\lambda = 0.614 \times 10^{-8}$ cm. for the mean wave-length of the $K\alpha$ radiation of rhodium[7] and gives for silver, $a = 4.11 \times 10^{-8}$ cm., and for gold, $a = 4.09 \times 10^{-8}$ cm. both slightly higher than the values here found. Hull's value for palladium, $a = 3.95 \times 10^{-8}$ cm. is also

[1] Mean of several concordant values, including both conditions, *R* and *RA*.

[2] Mean of two concordant values.

[3] R. T. Birge, PHYS. REV. (2), *14*, 361–368 (1919).

[4] L. Vegard, Phil. Mag., (6), *31*, 83–88 (1916). Ag.

[5] L. Vegard, Phil. Mag., (6), *32*, 65–95 (1916). Au.

[6] A. W. Hull, PHYS. REV., (2), 17, 571–588 (1921).

[7] W. Duane, loc. cit.

higher than those here determined by the same method, but he states that the lines on the photograph which he obtained were rather faint and diffuse, which in the light of the present study suggests inhomo-

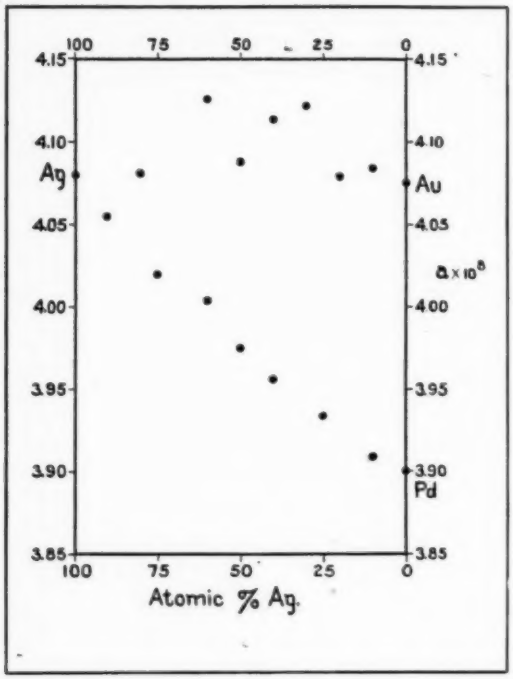


Fig. 1.

geneity. The presence of occluded hydrogen is a possible source of high values of a for this metal.[1]

Qualitative Results.

The variation in the parameter of the space-lattice is, to a first approximation, a linear function of the atomic per cent. of either component. There is, however, a tendency for the chemically unlike components, Ag and Pd, to be packed more closely than this, and a tendency for the components of widely differing mass, Ag and Au, to be packed less closely when mixed in certain proportions. Whether the correlation between the observed facts and the properties to which attention is invited by this choice of words is accidental or not cannot be determined from such meagre data.

The abnormally high values of a obtained for Ag_3Au_2, Ag_2Au_3, Ag_3Au_7 suggest that Tammann[2] is right in concluding that in the face-centered cubic arrangement of atoms solid solutions of the compositions A_3B,

[1] L. W. McKeehan, Amer. Phys. Soc. Washington Meeting, April, 1922.

[2] G. Tammann, Zs. f. anorg. u. allgem. Chem., *107*, 1–239 (1919).

AB, AB_3 are particularly symmetrical and homogeneous. The compositions of the abnormal members of the Ag-Au series fall between these points, and the alloy Ag-Au appears to be normal in its value of a. The high value for the alloy Ag_3Pd_2 may be due to the same effect, but the distance of this point from the smooth curve hardly exceeds the probable error in its position.

It should be mentioned that the method of measurement favors low values of a at the expense of high values, so that what is actually determined is the smallest a (and the largest density) possessed by a considerable fraction of the crystals. The sag in the Ag-Pd curve might accordingly be attributed to a greater variability in a for the intermediate members. The reason for preferring the hypothesis of increased interatomic attraction is that the bands are no broader and no more diffuse for those members of the series which give low values of a than for those which give high values, and no wider than the width of the sample requires.[1] In fact it is for the highest points on the Ag-Au curve that the difficulty of determining a is most increased by diffuseness in the bands. It is perhaps not irrelevant that the excess of the melting point over the annealing temperature is least in the Ag-Au series, so that diffusion may be more effective here than in the Ag-Pd series in preventing regular arrangements, even if once established, from persisting.

Recent work by Bain[2] indicates that the gradual variation in crystal structure here found occurs in other solid solution alloys. He also obtained evidence, in the case of Cu-Ni and Cu-Au alloys, of the special regularity of distribution at the critical compositions, A_3B and AB_3, predicted by Tammann.[3] No such evidence was obtained in this study, perhaps because Ag and Pd have atomic numbers too nearly equal to give a "reflection" due to their difference and because these particular compositions were missing from the Ag-Au series.

The high values of a frequently found in condition R cannot be the immediate result of the cold-working which the material has suffered, for they do not recur in condition RAR. They are accordingly ascribed to inhomogeneity, existing in the original ingot, in the arrangement of atoms within each crystal, which does not permit the interatomic forces between unlike atoms to have their maximum effect. It will not suffice to suppose that different crystals have different compositions, for, as stated above, those with the more compact arrangements would be the ones for which a would actually be measured. After annealing, which renders the individual crystals more homogeneous, as proven by the

[1] L. W. McKeehan, Frank. Inst. Jl., *193*, 231–242 (Feb., 1922).

[2] E. C. Bain, Min. and Met., Preprint 1139–N (Feb., 1922).

[3] G. Tammann, loc. cit.

better definition of the diffracted images of the source, the effect of cold-working is only to break up the existing homogeneous space-lattice into smaller units, and to shear and displace these fragments into less isotropic arrangements. The increase in intercrystalline area, and in the number of atoms thereon which do not fit into both the adjacent space-lattices, would account for the normal decrease in average density associated with cold-working where there is much shear. If working is so severe, however, that the space-lattice is destroyed throughout considerable volumes it is possible that some segregation of the components can occur at the same time. Subsequent crystallization may then leave the components less well mixed than before this severe working, and thus give rise to crystals with abnormal values of a. Some of the Ag-Au alloys were rolled until brittle, and in this condition gave hardly any evidence of crystalline structure, which would represent the end of the first stage in the supposed process. As noted above, recrystallization is particularly slow in the case of Ag-Au alloys, so that no attempt was made to reëstablish the crystal structure in these samples, especially since, if the supposed segregation exists, heating in this condition would change the composition by evaporation of silver.

The relative volatility of silver, mentioned in the last paragraph, is a possible source of error in the composition of the alloys, and this, particularly in the Ag-Pd series, might vitiate the conclusions as to the dependence of a upon the composition by changing the latter to an unknown extent. In order to estimate the possible effect of this volatility a sample of the alloy AgPd was repeatedly annealed at 870° C. for periods of 2 hours. No change in the value of a indicating a progressive change in composition could, however, be detected, so that any error due to this cause is negligible.

In conclusion I desire to express my indebtedness to my colleague Dr. E. F. Kingsbury, who placed at my disposal his first-hand knowledge of certain physical and chemical characteristics of the alloys here studied which suggested or confirmed the conclusions here presented.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY AND THE
WESTERN ELECTRIC COMPANY, INCORPORATED, NEW YORK,
June 12, 1922.

DETECTING EFFICIENCY OF THE RESISTANCE-CAPACITY COUPLED AMPLIFIER TO 6,000 METERS.

BY W. G. BROMBACHER.

SYNOPSIS.

Detecting Efficiency and Current Amplification of the Resistance-capacity Coupled, Two-tube Amplifier.—Test of Hulburt's formula, giving a relation between detecting efficiency and the constants of the tubes and circuits, has been extended to 6,000 meters. The detecting efficiency is defined as b_0/A^2, where A and b_0 are the amplitudes, respectively, of the input grid potential and of the rectified component of the output plate current. It was found that (1) for any wave-length the relation between b_0 and A^2 is linear; (2) for constant wave-length, b_0/A^2 varied with the coupling capacity in accordance with the formula within about 10 per cent., being practically constant for capacities greater than 200 $\mu\mu$ F; (3) for constant capacities, b_0/A^2 varied with wave-length for ranges 1,100 to 2,500 and 2,500 to 6,000 meters in fair agreement with the theoretical curve. The current amplification, $n = b_0/Eg^2$, where Eg is the amplitude of the potential impressed on the grid of the second tube, was found to be independent of the wave-length to 6,000 meters.

Plate current of vacuum tube (Radiatron UV 201) was found to be *sensitive to the external temperature.*

1. INTRODUCTORY.

The detecting efficiency of the resistance-capacity coupled electron tube amplifier has been discussed by E. O. Hulburt.[1] He derived a formula which indicated the connection between it and the constants of the electron tubes and the coupling circuits. His experiments showed that the theoretical relation held in the region from 400 to 1,600 meters.

The detecting efficiency was defined by the relation $\lim_{A \to 0} \frac{b_0}{A^2}$, in which A and b_0 are the amplitudes, respectively, of the input grid potential and of the rectified component of the output plate current.

Consider the high frequency amplifier of two tubes as shown in Fig. 1.

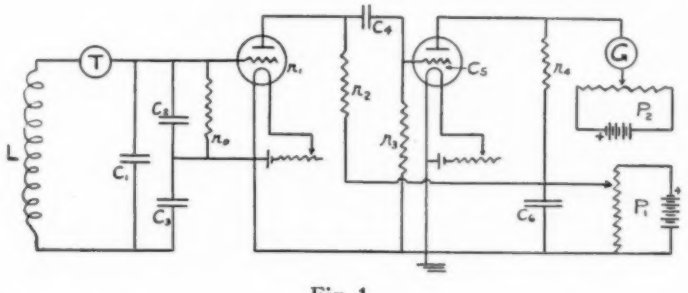


Fig. 1.

[1] PHYS. REV., 18, 165, 1921.

For this type of amplifier Hulburt derived the following formula, subject to the conditions that there be no rectification in the first tube and no grid filament current in the second tube

$$\frac{b_0}{A^2} = nk^2 g_1^2 \frac{(g_2g_3 - x_4x_5)^2 + [x_4(g_2 + g_3) + x_5g_2]^2}{(g_2g_3 - x_4x_5 + g_1g_3)^2 + [x_4(g_1 + g_2 + g_3) + x_5(g_1 + g_2)]^2} \Bigg/ \left(g_2 + g_3 + \frac{x_5}{x_4}g_2\right)^2 + \left(x_5 - \frac{g_2g_3}{x_4}\right)^2 \quad (1)$$

in which A is the amplitude of the radio frequency potential impressed on the grid of the first tube, b_0 is the rectified component of the resulting radio frequency current in the plate circuit of the second tube; k is the amplification constant of the first tube. r_1 is the internal resistance of the first tube from filament to plate. C_5 is the filament-grid capacity of the second tube. Resistances r_2 and r_3 and capacity C_4 are as shown in Fig. 1.

Let $\omega/2\pi$ be the frequency of the impressed voltage.

Let

$$\frac{1}{r_1} = g_1, \qquad \omega C_4 = X_4,$$

$$\frac{1}{r_2} = g_2, \qquad \omega C_5 = X_5.$$

$$\frac{1}{r_3} = g_3,$$

One term has not been defined, which is

$$n \equiv \frac{b_0}{E_g^2},$$

where E_g is the amplitude of potential impressed on the grid of the second tube. n does not depend on the frequency of the impressed voltage. (See Fig. 6.)

Let

$$g_2g_3 - x_4x_5 = a,$$
$$x_4(g_2 + g_3) + x_5g_2 = b.$$

Then, more accurately, the formula may be written

$$\frac{b_0}{A^2} = nk^2 g_1^2 \frac{a(a + g_1g_3) + b(b + x_4g_1 + x_5g_1)}{(a + g_1g_3)^2(b + x_4g_1 + x_5g_1)^2} \Bigg/ \left(g_2 + g_3 + \frac{x_5}{x_4}g_2\right)^2 + \left(x_5 - \frac{g_2g_3}{x_4}\right)^2. \quad (2)$$

It is to be noticed that this formula gives the detecting efficiency in terms

of the constants of the electron tubes and the coupling circuits. Also Formula (1) is an approximation of (2), the use of which is justified under obvious conditions.

The object of this paper is to make the experimental measurements necessary in order to test Formula (1) for long wave-lengths, and to this end measurements were made from 1,000 to 6,200 meters.

2. APPARATUS.

The apparatus consisted of a condenser potential divider, the amplifier and a D'Arsonval galvanometer. The arrangement is essentially that of Fig. 1. The potential divider consisted of the coil L, the Weston thermo-galvanometer T, and the condensers C_1, C_2 and C_3. This apparatus has been previously described by Hulburt and Breit.[1] The potential impressed on the grid of first tube may be found from

$$A = \frac{C_3 I}{\omega(C_1C_2 + C_1C_3 + C_2C_3)}, \qquad (3)$$

in which I is the effective current measured by T. By coupling L to a suitable electron tube generating set, unmodulated high-frequency voltage of a small known amplitude and frequency was impressed on the grid of the first tube. The high-resistance leak r_0 was connected across C_2 to insure a definite value of the grid potential during the experiment. The effect of r_0 upon the impedance of C_2 was negligible because C_2 was large (either .05, .1, or .2 MF) and the frequencies used were of the order of 10^5.

The amplifier was a two-tube one with resistance capacity coupling. The tubes were General Electric Company tubes, Radiatron type UV 201; they were used with the filament current of .94 ampere and had a common plate voltage supply of 52.3 volts. Separate storage cells supplied each filament. The plate current was found to be sensitive to external temperature changes, an effect explained, perhaps, by the fluctuation in the amount of the absorbed gases in the glass walls of the tubes. It was therefore found necessary to enclose the electron tubes in covered cardboard tubes in order to keep their temperatures constant. The plate battery was shunted by a 1.75 MF condenser C_6. The resistance r_2 was 115×10^3 ohms and r_3 was 360×10^3 ohms. The resistances r_0, r_2 and r_3 were non-inductive, being of the type described by Hulburt.[2] These were found to give satisfactory service. The value of the resistance for high-frequency currents was assumed the same as that measured with direct current.

[1] PHYS. REV., 16, 274, 1920.

[2] Loc. cit.

The change in the value of the rectified high-frequency component of the plate current of the second tube of the amplifier, designated by b_0, was measured by a D'Arsonval galvanometer, G, Fig. 1, connected across a resistance r_4 placed in the plate circuit. r_4 was 60,000 ohms. The galvanometer had a resistance of 9.0 ohms and a sensibility of 5.8×10^{-8} amperes per millimeter deflection on a scale 125 cms. distant. P_1 and P_2, Fig. 1, were potential dividers, P_1 serving to keep the plate voltage at the desired value, and P_2 to compensate for the potential drop in the resistance r_4 so that the galvanometer rested approximately at zero. When the grid voltage of the first tube was changed, a deflection of the galvanometer resulted which was proportional to the change in the rectified high-frequency component of the output plate current.

It was important that the filament currents remain constant. Any change in these currents resulted in a shift of the operating point of the tubes. The electron tubes were seasoned before every series of readings until a reasonably constant condition of filament current and electron emission was reached. In order to eliminate the error due to the usual slow drift of the galvanometer, the two zero readings were averaged. It was found that the grid leak r_0 gave a constant potential of nearly zero on the grid of the first tube when its value was 246×10^3 ohms. This value was not critical. For large values of r_0, the value of the grid potential shifted when it was necessary to vary the value of C_3. A Kolster decremeter, calibrated by the Bureau of Standards, was used to determine the wave-lengths of the high-frequency current.

3. Variation of Coupling Capacity.

The reading of the coupling condenser C_4 was varied at each reading, a number of input potentials were impressed on the grid of the first tube and the corresponding galvanometer deflections were noted. From the reading of T, the thermo-galvanometer, and a knowledge of the capacities C_1, C_2 and C_3, the amplitude of the change of the input grid voltage A was computed, using formula (3). Three sets of readings were taken, at wave-lengths 1016, 3070 and 6235 meters. The resulting curves with b_0 the ordinates and A^2 the abscissa, are shown in Figs. 2, 3 and 4. It can be seen that for each value of C_4 for all three wave-lengths the $b_0 - A^2$ curves are straight lines. This fact has been established by a large number of similar curves, not shown here. The curves for any one wave-length are plotted from data taken with the potential divider condensers C_2 and C_3 held constant. A change in the value of C_3 caused the curve for any particular value of C_4 to shift and also to change its slope. This is shown in Fig. 3 by the curve marked 628′. This fact

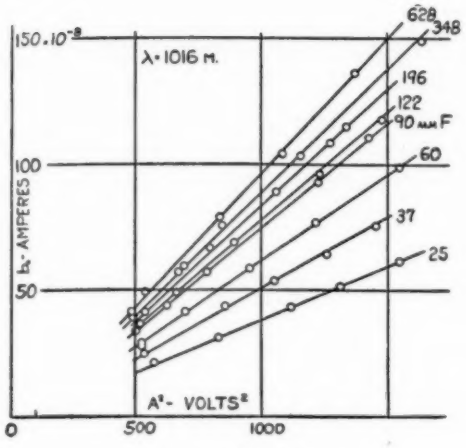


Fig. 2.

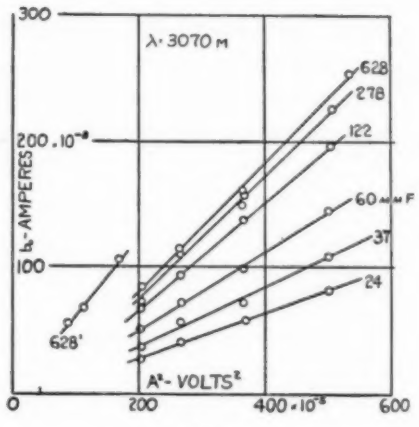


Fig. 3.

can be explained by a shift in the operating point of the first tube because of a shift in the normal value of the grid potential. r_0 had the value

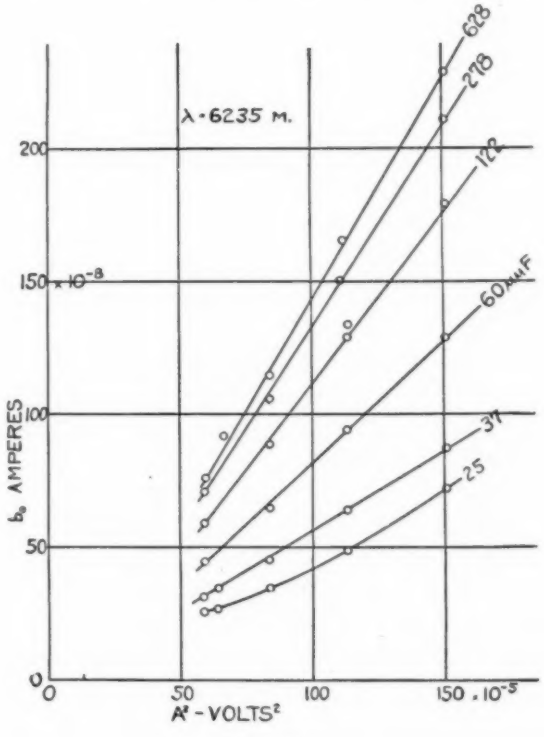


Fig. 4.

13×10^5 ohms during these readings. Another point of interest in these curves is that the straight lines do not pass through the origin, although

within the limit of experimental error they pass through a common point on the A^2 axis. This seems to indicate a constant error in the determination of A^2 although a check up of the calibrations revealed no differences large enough for compensation. It is also of interest to notice that for each wave-length there is practically the same current range (b_0) but that there is a large range in the value of A^2; for 1016 meters, .006 to .015; for 3070 meters, .002 to .005 and for 6235 meters, .0006 to .0015 volt^2.

The main fact, however, remains that the straight lines were obtained, as is predicted by formula (1).

In order to further test formula (1) the slopes of the curves corresponding to each value of C_4 were determined and then plotted against values of C_4 for each of the three wave-lengths as shown in Fig. 5. That

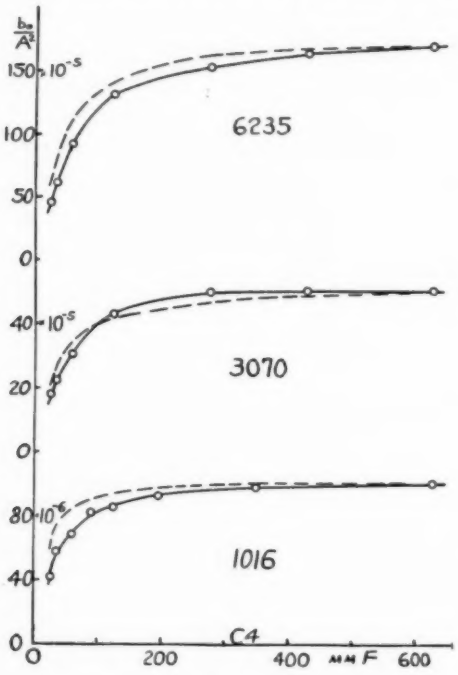


Fig. 5.

is, experimental values of b_0/A^2 are plotted against values of C_4. Then, from formula (1) the theoretical value was computed. Values of the constants not before given, r_1, the direct-current filament to plate resistance of the first tube, was 60×10^3 ohms; C_5, the filament-grid capacity of the second tube, was 18 MMF. This was measured in its socket and included the capacity of its lead wires, which were short, however. As neither n or k were determined experimentally, the computed curve was made to coincide with the experimental curve at C_4

equal to 628 MMF. The computed curves are the broken lines. While the agreement between the experimental and computed curve is not exact, it is quite satisfactory, revealing no marked differences in behavior for two of the wave-lengths considered, while for wave-length 3,070 m. the agreement is good.

No change in the character of the computed curve was found whether formula (2) or its approximation (1) was used.

4. VARIATION OF WAVE-LENGTH.

The coupling capacity C_4 was kept at its maximum value of 628 MMF, r_2, r_3 and r_4 remained at their former values of 115×10^3, 360×10^3 and 60×10^3 ohms. A series of readings were taken so that the variation of detecting efficiency with wave-length could be determined. The experimental results are given in the full line curve of Fig. 6.

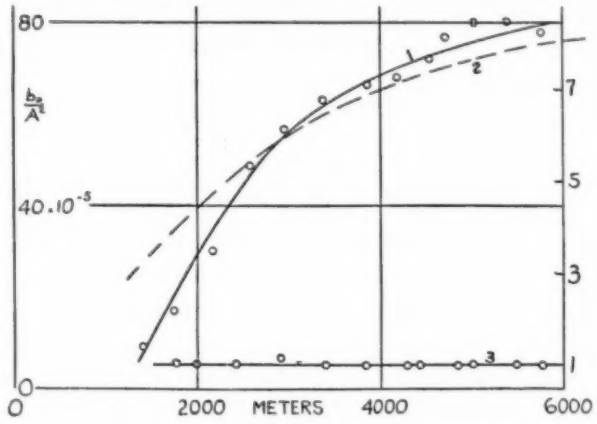


Fig. 6.

As the curve connecting the square of the input grid potential and the rectified component of output plate current does not pass through the origin, a series of readings was taken at each wave-length, a curve drawn and the slope determined. This slope is b_0/A^2. The experimental curves just mentioned were straight lines within experimental error.

In order to keep the grid potential of the first tube constant for the entire range of wave-lengths used, it was found necessary to fix its value near zero, which was done by making r_0 equal 246×10^3 ohms. This was tested by obtaining the deflection of the galvanometer when the condenser C_2 was short circuited, there being no high-frequency current in the input circuits. This test was made when the condensers C_1 and C_3 had values corresponding to the range of wave-lengths used. C_2 was 0.2 MMF throughout the run.

The computed curve, shown dotted in Fig. 6, was made to agree with the experimental curve in the neighborhood of 2900 meters. It was

computed from formula (2), as the approximate formula (1) differed with it over the range of wave-lengths computed.

The agreement of the two curves is substantial above 2,500 meters, and, it is believed, would be even better, if the apparatus had been used with better control over the grid potentials. The poor agreement at lower wave-lengths is due to the difficulty of keeping conditions constant for the entire range of observations. An unpublished curve, detecting efficiency against wave-length, for the region between 2,500–1,100 meters gives a straight line of about the same slope as the theoretical curve. This is in agreement with the straight-line relation obtained by Hulburt between 600–1,600 meters. Thus, the simple theory underlying Hulburt's formula is in agreement with experiments thus far made.

It is seen that the detecting efficiency at higher wave-lengths (lower frequencies) becomes independent of the wave-length.

5. AMPLIFICATION.

It was necessary to test the independence of n with respect to wave-length. By definition

$$n \equiv \frac{b_0}{E_g^2},$$

where b_0 is the rectified component of the output plate current and E_g is the amplitude of the potential variation on the grid of the second tube.

In order to measure n the input voltage was impressed directly on the second tube, the first tube being disconnected, and the output plate current was found for a series of wave-lengths. As before, sufficient observations were made for each wave-length so that a curve could be drawn and the slope determined. The slope was b_0/E_g^2. The curves so determined were straight lines. n was found to be sensibly constant for all wave-lengths as is shown in Curve 3, Fig. 6.

If the ordinate of Curve 1 be divided by the ordinate of Curve 3 at the same wave-length, both of Fig. 6, the quotient is the amplification of the current obtained by the use of the amplifying electron tube. That is, the quotient gives the number of times the rectified component of the plate current, b_0, is increased by the use of two tubes instead of one. The quotients, or current amplifications, are the ordinates on the right margin of Fig. 6. If telephones are used the sound intensity amplification is proportional to the square of these numbers.

This problem was suggested to me by Dr. E. O. Hulburt, now at the State University of Iowa, who derived the formula underlying the investigation.

JOHNS HOPKINS UNIVERSITY,
June, 1922.

THE THERMOELECTROMOTIVE FORCE OF COPPER-MANGANESE ALLOYS.

BY SKEZUG KIMURA AND ZUNEHACHI ISAWA.

SYNOPSIS.

Thermoelectromotive Force of Alloys of Copper with 5 to 23 Per Cent. Manganese for the Range 0° to 100° C.—The alloys were prepared from electrolytic copper and thermite manganese but contained as impurity about one fiftieth as much iron as manganese. The alloys were cast and then drawn to fine wires. After they had been annealed at 200° C. for 8 hours, the thermoelectromotive forces against fine pure copper wire were determined for various temperatures of the hot junction up to 100° C. The curves, as usual, correspond to the equation $E = \alpha t + \beta t^2$. For $t = 100°$ C., E is positive for all the alloys, especially if allowance is made for the effect of the iron content, though practically zero for alloys with less than 10 per cent. Mn. The alloys as cast and as drawn were more positive than after annealing. However, E showed negative values for the lower manganese alloys and for the lower temperatures, especially when the iron content was increased. In fact, though α is probably positive for all pure Cu-Mn alloys, *the effect of small percentages of iron*, carefully studied to 2 per cent. with a series of 30 alloys, was found to be to decrease α so that for 13 per cent. Mn and more than 0.50 per cent. Fe and for less than 11 per cent. Mn and more than 0.20 per cent. Fe, α is negative. On the other hand β is always positive but tends to decrease as the percentage of Mn is increased. Two alloys indicated that the *effect of 2 per cent. nickel* is to decrease α nearly as much as an equal amount of iron. *The effect of aluminum* seems to be the reverse but the five alloys tested did not give consistent results. *Ordinary manganese* contains just enough iron as impurity to make its E slightly negative at ordinary temperatures but adding 1 per cent. more iron, as suggested by Hunter and Bacon, would lower it too much.

Discussion of Electron Theory of Thermoelectromotive Force.—The electron theory does not account for the fact that E is positive rather than negative for Cu-Mn alloys against Cu, and that while Fe itself is positive against Cu its effect on E for these alloys is negative. It is suggested that the effect of atomic and molecular forces on the free electrons will have to be taken into account.

A KNOWLEDGE of the thermoelectromotive force of copper-manganese alloys and the way in which it is influenced by admixtures of other elements such as iron, nickel and aluminum is important because one or more of these alloys is widely used as standards for resistance. The data on this point being insufficient and somewhat contradictory, it was decided to study carefully the thermoelectromotive force of a large number of copper-manganese alloys.

In preparing the sample throughout this investigation electrolytic copper and thermit manganese were used and the metals were alloyed in Tammann tube furnaces. To protect from oxidation the necessary

quantity of barium chloride was first melted in the furnaces and the metals to be alloyed were charged in convenient order into them. Then the melted alloys were poured into porcelain tube crucibles which had been preheated to about 500° C. and the ingots were slowly cooled. An ingot about 10 cms. long and 1.8 cms. thick thus obtained, was annealed at 800° C. for 30 min. and then drawn into a wire the diameter of which was about 5 mm. This wire was drawn cold in the usual manner. The diameter of the wire was reduced two numbers (B. & S.) with one drawing to gauge number 13 and after that was reduced only one number at each drawing. Until the diameter of the wire reached its final value, it was annealed several times for 8 hrs. in an oil bath at 200° C. All the specimens used for this investigation were in the form of wire (B. & S.).

After the specimen had been once more annealed at 200° C. for 8 hrs. in the oil bath, its mean thermoelectromotive force between 0° and 100° C. was measured against pure, fine copper wire. The hot junction of the thermoelement, consisting of the specimen and the pure copper wire, was kept in a hypsometer and the cold junction in an ice bath. Of course, the usual expression "mean thermoelectromotive force over a certain range of temperature" has no meaning for a thermoelement for which the thermoelectromotive force varies with the temperature so as to have a minimum or a maximum within the range. Some samples of copper-manganese alloys correspond to this case. For simplicity, however, the mean thermoelectromotive force was measured at first as usual. For the measurement of the thermoelectromotive force a Rap potentiometer made by Siemens and Halske and a d'Arsonval galvanometer made by Leeds and Northrup were used.

The results are summarized in Table I. and are also plotted in curve *E* of Fig. 1. For most of the specimens the quantity was insufficient to allow the small percentage of iron in them to be determined by analysis. But as all specimens were made from the same materials by the same treatment, the content of iron in them may be presumed to be of the same order as in the case of those specimens whose iron content could be determined by quantitative analysis.

From these results it will be seen that the mean thermoelectromotive force of copper-manganese alloys between 0° and 100° C. at least when the manganese content is between 5 and 25 per cent., is certainly positive against copper and that within the same limit of manganese content, the greater the proportion of manganese the greater is the thermo-electromotive force. Our results at this point confirm those of Feussner and Lindeck.[1] It is true that in Table I. there may be seen a few samples

[1] Feussner and Lindeck, Abh. Phys. Tech. Reichsanstalt, 2, 515.

giving negative thermoelectromotive forces which casts a doubt on our conclusion. If Nos. 89, 102, 99 and 91 are considered, it will be noticed that even among samples with nearly the same percentage of manganese

TABLE I.

Manganese Content and Mean Thermoelectromotive Force.

No. of Specimens.	Cu. (Per Cent.)	Mn. (Per Cent.)	Fe. (Per Cent.)	E/° C. (Micro-V.)	E'/° C. (Micro-V.)
84.....	94.37	5.42	——	+ 0.03	+ 0.38
85.....	92.74	6.97	0.133	− 0.04	+ 0.45
94.....	91.85	8.04	——	− 0.01	+ 0.57
112.....	90.29	9.52	——	+ 0.34	+ 1.24
100.....	89.31	10.44	0.150	+ 0.02	+ 0.72
88.....	89.26	10.45	0.150	+ 0.22	+ 1.04
89.....	88.44	11.33	——	+ 0.38	+ 1.25
102.....	88.40	11.46	0.170	+ 0.20	+ 1.02
99.....	88.18	11.51	——	− 0.03	+ 0.61
91.....	88.18	11.62	——	+ 0.12	+ 1.03
97.....	87.30	12.40	——	+ 0.52	+ 1.48
101.....	86.21	13.58	——	+ 0.50	+ 1.45
103.....	86.07	13.65	——	+ 0.54	+ 1.50
90.....	85.64	14.24	——	+ 0.65	+ 1.70
93.....	83.50	16.29	0.290	+ 0.74	+ 1.85
95.....	82.65	17.03	0.330	+ 0.78	+ 1.65
86.....	82.11	17.58	——	+ 1.17	+ 2.10
96.....	79.56	20.12	——	+ 1.73	+ 2.68
98.....	77.05	22.52	——	+ 1.74	+ 2.58

there are very large irregularities in the thermoelectromotive force. According to our experiments a small percentage of such impurities as iron, nickel and chromium can easily cause the lowering of the thermoelectromotive force. Judging from curve E of Fig. 1 drawn through all

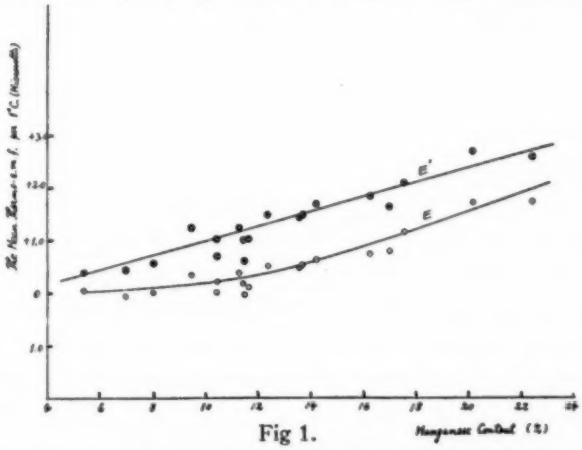


Fig 1.

Manganese content and mean thermoelectromotive force per 1° C. between 0° and 100° C. Curve E' for wires as drawn and curve E for wires after annealing.

the experimental points, No. 99 which gives a slight negative value may be considered an abnormal value due to the above cause. But this simple explanation is not sufficient to prove that the thermoelectromotive forces of the samples Nos. 89, 102 and 91 are nearer to the normal value than the thermoelectromotive force of No. 99, because if there are other reasons for raising the thermoelectromotive force of these samples, the opposite may equally well be concluded. For instance it was observed that the cast samples, even when they had been cooled at moderate speed, sometimes gave higher thermoelectromotive forces than those given by the same annealed samples. Curves I. and II. of Fig. 2 represent

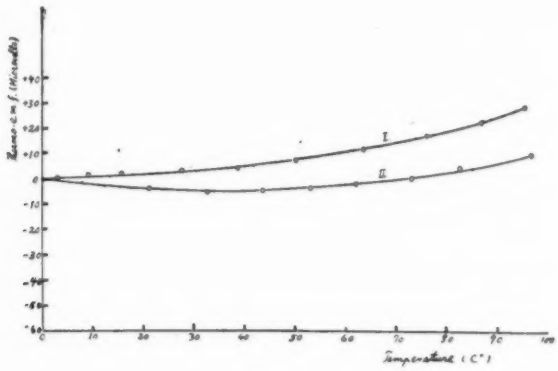


Fig. 2.

Thermoelectromotive forces of a copper-manganese alloy before and after annealing. Curve I. before annealing. Curve II. after annealing.

the thermoelectromotive force of a rod of copper-manganese alloy just cast and the same rod after annealing.

The effect of cold drawing must be taken into consideration as another cause of an increase in thermoelectromotive force. The value of the thermoelectromotive force represented by E' in Table I. and by E' in Fig. 1 are those obtained for samples just drawn, the corresponding values of the thermoelectromotive force for the same samples after annealing being represented by E in the same table and figure. It is, therefore, uncertain which value of the thermoelectromotive force, that of sample No. 99 or that of one of the samples Nos. 89, 102 and 91 is nearer the normal value. But if the state of the samples which gave the value of the thermoelectromotive force represented by curve E can be said to be normal, that is if the effect of the manufacturing process in our laboratory upon the majority of these samples can be said to be normal, then such samples as No. 99 can be considered abnormal. Iron may be considered as one of the causes of this abnormality.

THERMOELECTROMOTIVE FORCE PER UNIT DIFFERENCE IN TEMPERATURE.

In the previous section the mean thermoelectromotive force of copper-manganese alloys between 0° and 100° C. was found to be decisively positive against copper. Since the mean thermoelectromotive force is meaningless when the thermoelectromotive force per unit difference in temperature changes its sign between the two given limits of temperature, the variation of the thermoelectromotive force between 0° and 100° C. was studied for small temperature intervals. The hot junctions of the thermoelements were kept in an oil bath instead of in a hypsometer as in the preceding experiment. The oil bath was gradually heated by two incandescent lamps immersed in it and the temperature of the oil was kept uniform by means of a pump. The potentiometer was so adjusted that one division of the end dial just corresponded to one microvolt and a highly sensitive Thomson galvanometer was used for balancing.

The samples as before were in the form of wires and the results of their chemical analyses are shown in Table II. The iron in these samples

TABLE II.

No. of Specimens.	Cu. (Per Cent.)	Mn. (Per Cent.)	Fe. (Per Cent.)	Ni. (Per Cent.)
184.....	94.318	5.198	0.1416	
185.....	94.833	5.002	0.1416	
186.....	91.541	7.920	0.1770	
187.....	91.541	8.003	0.1947	
188.....	88.196	11.575	0.1947	
189.....	89.182	10.147	0.1947	
190.....	87.103	12.292	0.2655	
191.....	86.842	12.540	0.2832	
192.....	83.774	15.840	0.3009	
193.....	82.996	16.253	0.3186	
195.....	86.337	11.673	0.168	1.830
197.....	85.556	11.424	0.186	2.616

is merely due to the impurity in the manganese. The results of the experiments on these samples have been plotted in Fig. 3. The values of α and β in the formula of the thermoelectromotive force, $E = \alpha t + \beta t^2$, have been calculated and plotted in Figs. 4, 5 and 6.[1] It is seen from these curves that α is negative for samples of lower manganese content and positive for those of higher manganese content, while β is always positive. The relation between α and the percentage of iron for various concentrations of manganese is brought out in Fig. 4 and the relation

[1] Computed from the curves for $t = 40°$ and $t = 80°$ C.

between β and the concentration of iron in Fig. 5. The variation of α with the concentration of manganese for different percentages of iron in the alloy has been represented in Fig. 6.

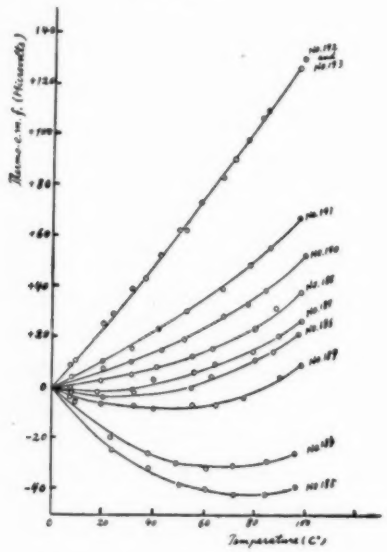


Fig. 3.

Manganese content and the temperature variation of the thermoelectromotive force as a function of the temperature of the hot junction.

In our opinion the difference between the curves in Fig. 3 is due to the fact that the effect of iron on the thermoelectromotive force varies widely with the proportions of copper and manganese. The samples Nos.

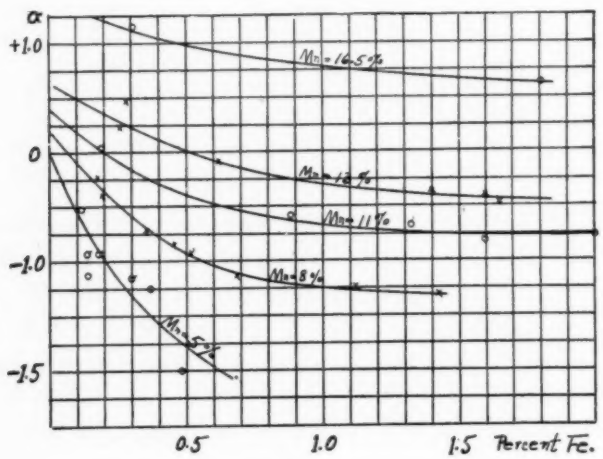


Fig. 4.

The variation of α in the equation, $E = \alpha t + \beta t^2$, as a function of the concentration of iron.

184 and 185 show exceptional negative thermoelectromotive forces and these results seem inconsistent with those obtained for sample No. 84 in Table I. Perhaps this discrepancy may also be attributed to the difference in the quantity of iron as an impurity. Though the above

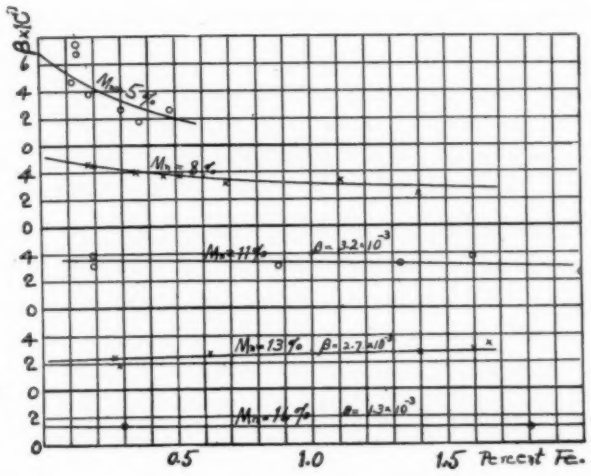


Fig. 5.

The variation of α in the equation, $E = \alpha t + \beta t^2$, as a function of the concentration of manganese.

conclusion is very probable, further investigation will be necessary as to the thermoelectromotive forces of copper-manganese alloys in which the manganese content is less than about 6 per cent.

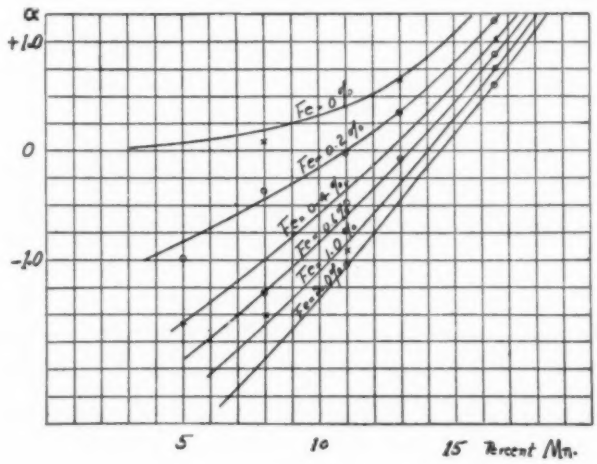


Fig. 6.

The variation of β in the equation, $E = \alpha t + \beta t^2$, as a function of the concentration of iron.

EFFECT OF NICKEL, IRON AND ALUMINUM ON THERMOELECTROMOTIVE FORCES OF COPPER-MANGANESE ALLOYS.

According to Feussner and Lindeck the positiveness of the sign of the thermoelectromotive force of copper-manganese alloys against copper can be annulled by the addition of a small quantity of nickel. For example, in a sample of about 12 per cent. manganese, about 2 per cent. nickel was suggested for this purpose.

It has already been seen that even though the mean thermoelectromotive force of copper-manganese alloys has a considerable positive value, dE/dt may not always be positive at ordinary temperatures. If attention is directed to the thermoelectromotive force of sample No. 189, it is seen that the mean thermoelectromotive force is about + 0.13 microvolt per degree Centigrade. But dE/dt for the same sample is negative for any temperature less than about 18° C. and it becomes zero at about 20° C. Thus it will be seen that copper-manganese alloys containing the same order of manganese as that in the ordinary manganin have a very small temperature coefficient of the thermoelectromotive force against copper at ordinary temperatures and that at lower temperature dE/dt becomes negative. If a small percentage of nickel is added to these samples, the thermoelectromotive force has a very large negative value at room temperature. This fact is clearly seen in samples of manganin wire on the market as well as those prepared in our laboratory (Fig. 7).

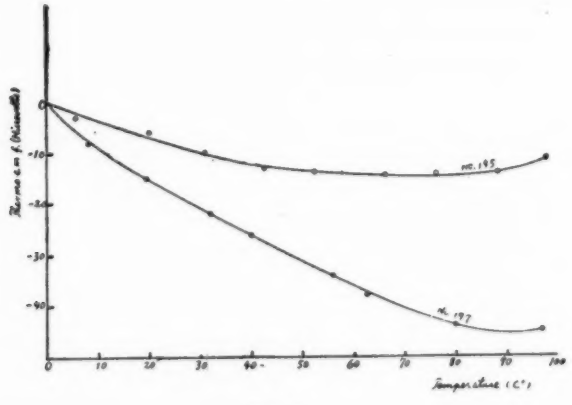


Fig. 7.

The effect of nickel on the thermoelectromotive force of a copper-manganese alloy containing about 11.5 per cent. manganese, as a function of the temperature of the hot junction.

It is thus seen that aside from its influence on the temperature coefficient of the resistance of manganin, the addition of nickel to manganin is not desirable where the manganin is to be used for standard resistances. Hence the idea of Feussner and Lindeck that nickel could be added to

manganin to cancel the positiveness of the sign of the thermoelectromotive force, is not satisfactory because the effect is too large.

When manganin was first made by Feussner and Lindeck the iron content was perhaps nothing but impurity which came from the manganese. But it has been proposed by Hunter and Bacon that about one per cent. of iron should be added to manganin to improve the temperature coefficient of the resistance. Although there will be difference of opinion about this suggestion, it is important to investigate the effect of the presence of iron on the thermoelectromotive force of copper-manganese alloys, because iron is always present as an impurity in manganese. One example of the results of our experiments in this connection is given in Fig. 8. The results of the chemical analyses of these samples are contained in Tables II. and III.

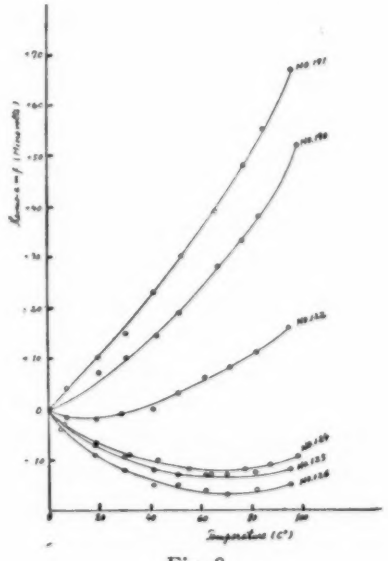


Fig. 8.

The effect of iron on the thermoelectromotive force of a copper-manganese alloy containing about 13 per cent. manganese as a function of the temperature of the hot junction.

Manganese Content and Mean Thermoelectromotive Force.

TABLE III.

Approx. Per Cent. Manganese.	No. of Specimen.	Copper, Per Cent.	Manganese, Per Cent.	Iron, Per Cent.
13.....	122	85.573	13.430	0.6195
	124	85.330	12.877	1.3983
	125	85.073	13.117	1.5930
	126	85.330	12.877	1.6544

From these results it must be concluded that a small percentage of iron can cause a considerable lowering of the thermoelectromotive force of copper-manganese alloys and that its effect is of the order of that of nickel or sometimes rather greater than that of nickel. As already pointed out the presence of iron as an impurity in manganin is sufficient to lower the thermoelectromotive force of copper-manganese alloys and that the intentional addition of nickel is unnecessary. Furthermore, Hunter and Bacon's proposal to add about one per cent. of iron, is not desirable for the purpose of minimizing the thermoelectromotive force of copper-manganese alloys, because one per cent. of iron is far too much.

Recently in discussing a paper by Bash, Weimer has stated that an alloy of 84.2 per cent. copper, 11.5 per cent. manganese and 4.2 per cent. aluminum is an ideal material for resistance standards. He points out as the valuable properties of this alloy that its thermoelectromotive force against copper is about one tenth of that of manganin and that the constancy of its resistance seems to be quite good, while its mechanical properties are considerably better than those of manganin. According to our experiments aluminum affects copper-manganese alloys so as to make the thermoelectromotive force slightly more positive. Thus if aluminum is added there will be no need of any precaution against an excessive lowering of the thermoelectromotive force as in the case of the addition of nickel. The aluminum will make it less probable that the iron as an impurity will produce a large thermoelectromotive force. In this respect it is safer to add aluminum than to add nickel. But in our opinion the intentional addition of aluminum will also be unnecessary for the purpose of minimizing the thermoelectromotive force. Samples of this new alloy having various percentages of aluminum were prepared in our laboratory and their thermoelectromotive forces measured. But as our samples seem not to be homogeneous, a more detailed study of these alloys will be left for a later investigation.

RELATION OF RESULTS TO ELECTRON THEORY OF THERMOELECTROMOTIVE FORCES.

Certain solid solutions have negative thermoelectromotive forces against their solvent metals, while other solid solutions have positive thermoelectromotive forces. Any theory of thermoelectromotive force which makes it necessary for the thermoelectromotive force of solid solutions against their solvent metals to have one sign in all cases, is unable to explain such experimental facts as were obtained in this investigation. The present electron theory which can not in its present form account for such a reversal of sign, does not therefore offer a satis-

factory explanation of these results. To make it possible for the electron theory to explain such results, it will be necessary to consider that atomic forces greatly affect the energy of free electrons and therefore the thermo-electromotive forces.

The Electrotechnical Laboratory,
Department of Communications,
Tôkyô.

NOTE ON OVERBLOWN PIPES.

PART I.

BY S. BHARGAVA AND R. N. GHOSH.

SYNOPSIS.

Minimum Pressures to Excite the Fundamental Note and Octave of a Pipe with Lip at Various Distances from the Edge.—It is well known that as the blowing pressure is increased first the fundamental is excited, then the octave appears, then after an interval of beating the octave alone is heard. With the pipe tested (fundamental pitch 490), as the lip distance was increased from 8 to 12 mm., the minimum pressures for the fundamental and octave, respectively, increased from 0.4 to 0.9 cm. and from 2 to 25 cm. of Hg.

Change of Pitch of a Pipe with Blowing Pressure.—This phenomenon is well known. For a particular pipe, studied with the help of phonodeik records, the fundamental pitch increased from 490 to 505 as the pressure was increased from 6 to 32 cm. of water. For 50 cm. of water the pitch (octave) was 1052.

THE experimental data necessary for working out the mathematical theory of the fluid motion near the mouth of an organ pipe seem to be wanting. Whatever accounts we have are scattered and incomplete. The present note describes a few quantitative results on (1) The variation of pitch with increase of pressure, (2) The minimum pressure necessary to excite the fundamental and the octave at various distances of the lip from the edge. The effect of the increase of the blowing pressure is to increase the pitch and the intensity, quantitative determinations of which are given in a paper in the PHYSICAL REVIEW.[1] The change in pitch with increase of pressure has been determined by the late Lord Rayleigh.[2] He employed resonators to determine the rise of pitch with increase of pressure. In order to be more accurate it was thought best to dispense with resonators and employ a photographic method for the determination of the pitch. For this purpose the record of the aërial vibration was obtained by a Phonodeik simultaneously with the trace of a vibrating fork on a sliding photographic plate. The frequency was determined by counting the number of waves. The following table shows a typical case.

The amount of variation in pitch is the same as observed by Lord Rayleigh. The important point to be noticed in the table below is the jumping of the pitch to the octave and, further, it must be noted that

[1] PHYSICAL REVIEW, Sept., 1920.

[2] Scientific Papers, Vol. II, p. 92.

the frequency at 38 cm. of water is double that of the note just at the next lower pressure. At about 30 cm. of water the octave is clearly heard with the fundamental. With the rise of pressure the octave

TABLE I.

Distance of Lip from Edge .8 cm.

Pressure in Water Column.	Frequency.
6 cm.	490 Fundamental
10 "	495
20 "	500
32 "	505
38 "	1050 Octave
50 "	1052

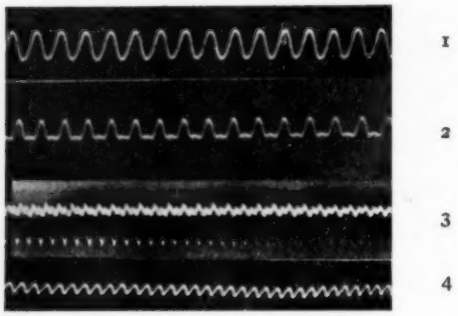
increases in prominence, and just before the note settles down to the octave only, there is beating as noticed by Raps,[1] Rayleigh and Lough.[2]

§ II. EXPERIMENTS WITH DIFFERENT POSITIONS OF LIP AND HIGH PRESSURES.

The lip was placed at different positions and made air tight. Compressed air was blown into the pipe, and the pressure near the mouth was recorded by a mercury manometer. It was found that the sequence of the phenomena is the same whatever be the position of the lip. The difference lies in the enormous pressure required to excite the pipe. We have observed in Table I. that the fundamental is elicited at a pressure of 6 cm. of water when the distance of the lip from the edge is about .8 cm. When the distance is 1.2 cm., the pressure necessary to excite the fundamental is 0.9 cm. of mercury (12.2 cm. of water). As the pressure is increased the pitch rises, but more slowly than the case when the lip was at .8 cm. from the edge. With the rise of pressure, the note develops its octave which is so strong that even an unaided ear cannot fail to detect it. As the pressure is further raised, the beat tone appears when on a slight increase of pressure the beat tone disappears, giving place to a steady octave. The necessary condition for obtaining the octave is the beat tone which is always obtained at a pressure depending upon the distance of the lip from the edge. Beyond the octave very little rise of pitch is obtained with increase of pressure. The addition of pressure increases the intensity considerably. In plate I. a few vibration curves which were obtained at high pressures are shown. Fig. 1 shows the fundamental, Figs. 2 and 3 show the gradual development of the octave clearly. Fig. 4 represents the octave which is more or less simple in character like the fundamental.

[1] Ann. der Phys., Vol. 1, p. 193.

[2] Phil. Mag., Jan., 1922, p. 72.



Figs. 1–4.

Fig. 5 shows the relation between the minimum pressures (ordinates in the figure) necessary to excite the fundamental at various positions of the lip. It will be observed that the minimum pressure increases slowly with increasing distance, then becomes rapid.

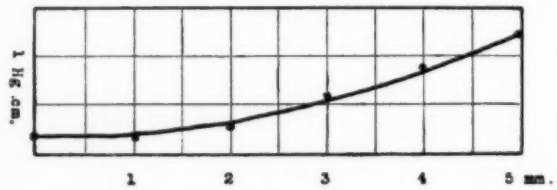


Fig. 5.

Origin representing .8 cm. from the edge.

Fig. 6 exhibits the relation between the pressure necessary to excite

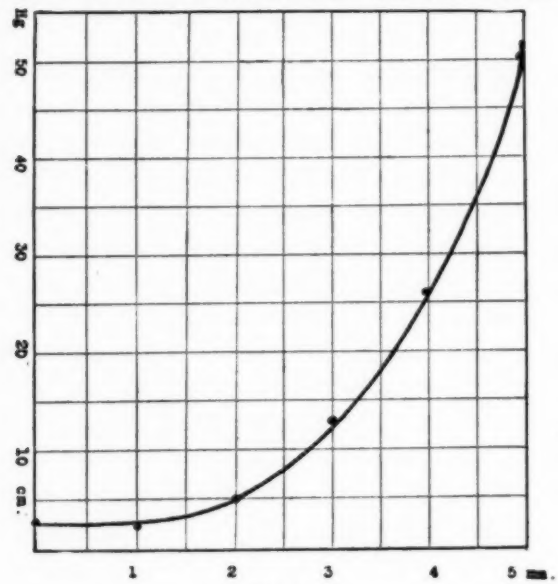


Fig. 6.

Distance of lip from the edge at the origin is .8 cm.

the octave at various positions of the lip. It is evident from the curve that the increase of pressure to change the note to the octave becomes greater as the lip distance increases. The curve is almost logarithmic to the distance axis.

§ III. Discussion of Results.

Since the rise of pitch with increase of pressure, the presence of the octave, and the beat tone, and finally the jumping to the octave, are quite general, *i.e.*, obtained at any position of the lip, it is evident that the hydrodynamical problem is quite definite. The fact that a certain minimum pressure is necessary to start the pipe, shows that the length of the air jet must be such as to allow it to flow past the edge. When the jet flows past the edge, it wafts to one side or the other delivering a puff at each journey. The maintenance is effected by the energy supplied by blowing. But this elementary view does not explain the gradual rise of pitch with increase of pressure. The effect of the increase of pressure is to produce a vortex motion whose effect is to diminish the effective inertia of the system, *i.e.*, the oscillating air jet, thus reducing the period. This qualitatively explains the rise of pitch. The presence of the octave and the beat tone can be explained on lines suggested by Lough.[1]

If we assume that the vortex motion has a certain natural period depending upon the pressure and decreasing with the increase of pressure then the phenomenon can be easily explained. Initially the period of the air jet is the same as that of the vortex pulsations. So that the two forces conspire, and produce the maximum effect. As the pressure rises, the period of the air jet decreases but more slowly than the pulsations, and in a short time they become discordant, when the fundamental is weakened. Finally the forces due to the pulsations excite in the pipe the next higher mode of vibration independently, *i.e.*, the octave, which becomes prominent, and the fundamental dies out. It will be observed from the above discussion that the pitch of the note on increase of pressure will jump to the octave of the note obtained at the next lower pressure.

MUIR CENTRAL COLLEGE,
ALLAHABAD, INDIA,
May, 1922.

[1] Lough, loc. cit.

THE ENERGY LOSSES ACCOMPANYING IONIZATION AND RESONANCE IN MERCURY VAPOR.

BY JOHN A. ELDRIDGE.

SYNOPSIS.

Energy Losses Accompanying Radiation and Ionization in Mercury Vapor.—To make possible a *direct determination* of the distribution of electron energies after impact with vapor molecules, a special tube was constructed in which the usual grid was replaced by two diaphragms each pierced with only a single hole. These divide the tube into two chambers which can be maintained at different pressures, the one in which the collisions take place being kept at a sufficiently high pressure and the other, in which the energies of the electrons after the collisions are measured, at a very low pressure by the use of liquid air. The source of electrons was an oxide-coated platinum foil heated by radiation from a tungsten filament, and energy distribution curves were obtained for a given accelerating potential by recording the electron current as a function of the retarding potential. These curves show that below 4.9 volts the collisions are elastic but that at higher voltages energy losses of 4.9, 5.7 or 6.7 volts may occur. For example, with an accelerating field (corrected) of 9 volts, breaks occur for retarding potentials of about 2.3, 3.3 and 4.1 volts, the curve being approximately horizontal between breaks. When ionization is produced, however, the electron loses all its energy, even though this much exceeds the ionizing potential, 10.4 volts, and the electron freed by the ionization also seems to have practically no energy. The 6.7 volt type of radiating collision is not probable unless the energy of the colliding electron exceeds 8.5 volts, but it becomes far more prominent than the 4.9 volt type above 10 volts. *Comparison with spectroscopic and photoelectric data.* The observed radiating potentials correspond to the known absorption lines λλ 2536 (4.9 volts), 2330 (5.3), 2140 (5.9) and 1849 (6.7). Apparent discrepancies between these results and photoelectric data are discussed but the explanation is not yet clear.

WHEN, in 1913 and 1914, Franck and Hertz published the results of their investigation concerning the nature of electron collisions with gas molecules, there already existed a theory which accorded well with their observations, and their work and that of the many others that have worked in this field during the last decade has resulted in modifying, amplifying, but, to a surprising extent, in confirming the quantum theory as applied to atomic structure and radiation. This theory has directed much of the work in this field to the determination of the exact values of ionizing and radiating potentials, and in the case of the metallic vapors the result has almost invariably been an admirable check between these values and those predicted (by the quantum theory) from the spectral frequencies. It is surprising that comparatively little has been attempted in the way of giving precision to our conception of what actually takes place at these critical potentials. The most sig-

nificant advance of this period was made when Davis and Goucher[1] showed that no ionization occurred at 4.9 volts in mercury. This changed and made much more interesting our picture of the phenomena, giving us two classes of critical potentials, the "resonating" and the ionizing potential. For the most part it has been so easy to fill in the hiatus left by experimentation with plausible extensions of the theory, that the gaps in the experimental evidence are not always apparent and yet a critical study of almost any of the investigations which have been published would show much that is not clear. Quantitative measurements are necessary before we can hope to solve all of these difficulties; yet some of the inconsistencies are so striking as to make us suspect some of the major tenets of our theory. Some of these difficulties formed the occasion for the present investigation, and as an introduction thereto it may be well to recall two recent studies of electronic collisions in mercury vapor.

In Fig. 1 is reproduced a curve, obtained by Mohler, Foote and

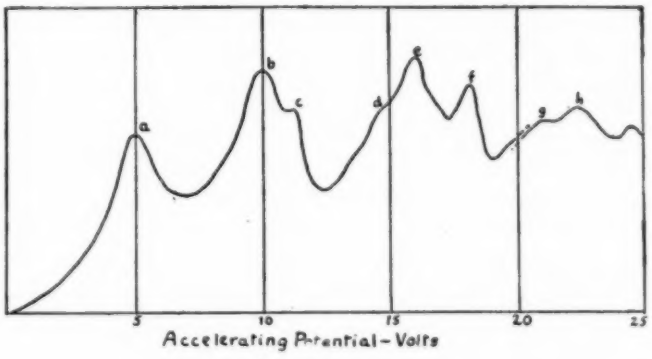


Fig. 1.

Meggers,[2] and in Fig. 2 one by Franck and Einsporn.[3] The experimental arrangements of these observers were quite similar. The electron was accelerated from the hot cathode to a first grid, then entered a constant potential region where most of the collisions were made, and was then slightly retarded from a second grid to the plate. The current to the plate is plotted as ordinate, and the accelerating potential as abscissa. The curves are in a general way similar, the differences which exist being presumably due to the extreme purity of the mercury and constancy of experimental conditions in the work of Franck and Einsporn.

Mohler, Foote and Meggers, interpreting their results, point out that

[1] PHYS. REV., 10, p. 101 (1917).
[2] Journal Opt. Soc., 4, p. 369 (1920).
[3] Zeit. der Phys., 2, p. 18 (1920).

all peaks which occur are to be explained as due to combinations of collisions of the 4.9 volt and 6.7 volt type. The inflections at *a*, *b*, and *d* are due to successive collisions of the first type; *c*, *f*, and *i* to one of the

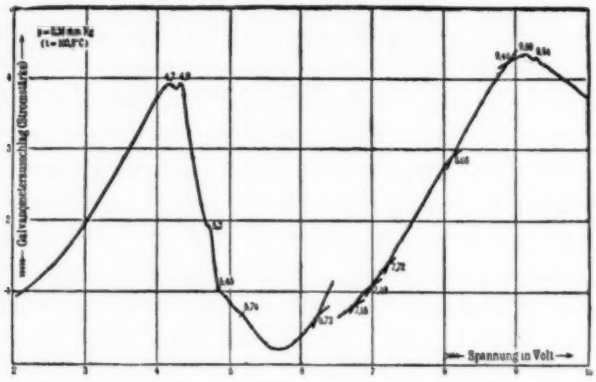


Fig. 2.

first type combined with one or more of the second; *e* and *h* to two of the first and one or two of the second; and *g* is due to three of the first and one of the second. The new type of collision (involving an energy loss of 6.7 volts) corresponds to the λ 1849 line of mercury. This line is a prominent absorption line, and while it has never been observed spectroscopically below the ionization point, photoelectric evidence that it did indeed appear at 6.7 volts had been adduced by Goucher.

Figure 1 gives strong evidence for the existence of the second type of collision with the 6.7 volt energy loss. The peaks of the curve occur at voltages which check quite closely with those obtainable from combinations of multiples of 4.9 and 6.7 volts, and all such combinations are represented *excepting 6.7 volts itself and its multiples*.[1]

Curves similar to the above, showing two resonance potentials, were obtained for other metals of the second group of the periodic table: cadmium, zinc, magnesium, and calcium; but again, except in the case of calcium, no peak was found corresponding to a single collision of the second type. To account for this it was supposed that the inflection which should have occurred here was hidden by the overlapping effect of the first resonance point. This seems an unlikely explanation since later peaks, though equally close, are readily distinguishable. Moreover, as has been noted, just as there is no peak corresponding to a single 6.7-volt collision in Fig. 1, so there is none corresponding to any simple multiple of this. And yet this type of collision when it appears in com-

[1] The agreement is not perfect. The interval between *b* and *c* and between *e* and *f* should be the same, *i.e.*, 1.8 volts, but the peak at *c* seems always to appear too soon.

bination with those of the 4.9-volt type gives very prominent peaks—peaks which are in fact more prominent than those corresponding to simple multiples of 4.9 volts, which beyond the second are quite weak.[1]

There can be, however, little question of the essential rightness of the interpretation of the peaks which occur in Fig. 1, but an explanation is needed which will account for the absence of the others and for the relative magnitudes of those which do occur. The following hypothesis, at the time it occurred to the writer, seemed to be somewhat doubtful, and yet to be the only one which would bring consistency to the above seemingly inconsistent facts: At potentials slightly above 6.7 volts, collisions of the 6.7-volt type may be possible, but are very improbable as compared with those of the 4.9-volt type. As the potential is raised, these collisions become more and more probable, and at high voltages are more likely to occur than those of the 4.9-volt type. Single 6.7-volt collisions will take place on this hypothesis if an electron has a large enough kinetic energy—say 9 or 10 volts, but these will not involve a *total* energy loss and the electron will still reach the anode; at potentials just above 6.7 volts practically no collisions of this type will occur. The usual experiment indicates only the points at which inelastic collisions involving total or almost total energy losses begin to take place, and will, therefore, give no indication of a single 6.7-volt collision. Similarly, simple multiples of this type of collision, though often occurring, will not be indicated, because, to be indicated on the curve, the last collision must be by an electron with kinetic energy of just 6.7 volts, and such an electron will lose 4.9 rather than 6.7 volts of energy. The same hypothesis makes the first collision of an electron with high velocity more probably one involving a loss of 6.7 than of 4.9 volts. This would mean that peaks corresponding to pure multiples of 4.9 volts should be relatively weak at high voltages, and Fig. 1 shows that above 9.8 volts this is indeed the case.

There are other difficulties which occur in analyzing such a curve, but they will not be dwelt upon. The interpretation of the rise in current just before c, followed by the extremely sudden drop at c, is not clear to the writer. The rise is probably due to ionization, and our ignorance of what happens at ionization is fairly complete.

Turning to the curve of Franck and Einsporn, it is seen that in a general way it corresponds to the curve dicsussed above, but shows other weaker inflection points which are attributed to other types of inelastic collisions. In the earlier part of this very interesting paper, these writers show that

[1] I have obtained curves quite similar to Fig. 1, but because of the difficulties mentioned, I was not able to convince myself at the time that they were indeed due to 6.7 volt collisions.

a photoelectric effect occurs not only at 4.9 and 6.7 volts, but at many other potentials corresponding, through the quantum relations, to prominent lines in the mercury spectrum, a result in startling agreement with the Bohr conception of radiation. The curve showing the photoelectric current as a function of the accelerating voltage is not reproduced here.

The Bohr theory leads us to expect inelastic collisions at the "radiating" potentials indicated on the photoelectric curve, and Fig. 2 shows the inelastic collisions which were found to occur. As interpreted by Franck and Einsporn, this curve does show inelastic collisions at most of the radiating potentials. It is surprising however that no agreement was found between the magnitudes of the breaks in the two curves. In Fig. 2 we find the break at 4.9 volts of predominating importance, and this has no parallel in the photoelectric curves which indicated an emission of radiation at 4.9 volts of quite the same order of intensity as formed at 4.7, 5.3, 6.7, etc. The breaks indicated in Fig. 2 are certainly in most cases very weak, and correspond at times to inflections upwards and again to downward inflections in a manner which seems quite unaccountable. Inelastic collisions should always lead to downward inflections, according to the usual interpretation of such curves. The peak at 4.7 volts is more definite. The rise by which it is followed (just before 4.9) is unexpected, but can be explained if we assume that the 4.7 collisions cease when the potential slightly exceeds the critical value. Here, as elsewhere in the interpretation of the curves, we must suppose that Franck and Einsporn had a very small velocity distribution.

When the apparatus is suitably arranged (with high vapor pressure and no constant potential region), many repetitions of the 4.9-volt type of collision can readily be obtained which show little decrease in sharpness as the number increases. It is not difficult to understand the absence of the 6.7 type of collision from such a curve, since the electron probably never gets a velocity enough in excess of 4.9 volts to excite this radiation, but it would be thought that the critical voltages which lie nearer to 4.9 would be indicated by a rapid flattening of the peaks as the number increased.

Such are some of the questions which are left unanswered by recent experimentation in this field. The answer to many of them seemed to be obtainable by a method somewhat different from that hitherto employed.

As remarked above, the method developed by Franck and Hertz and quite generally used with modifications since then, measuring, as it does, the current to a retarding plate as a function of the accelerating voltage, is only competent to show the potentials at which *total* losses of

energy *begin* to take place (complicated, above the ionization point, by the ionization current).[1] It seemed desirable to alter this method by keeping the accelerating potential constant and varying the retarding potential. For any given accelerating potential, it should be possible by such a method to measure the actual distribution of velocity which exists among the bombarding electrons after a considerable number of collisions with mercury vapor.

This method is a quite obvious deviation from the usual procedure, and was used by Franck and Hertz in their early work to show that the 4.9-volt maximum was due to an energy loss of the electron. Sponer,[2] in a paper which appeared after the present work was begun, has used a similar method and has made it yield very interesting results as to the probability of inelasticity at 4.7 and 4.9 volts. However, the tube used by these experimenters was of the usual filament-grid-plate design, and with such a tube the method is very greatly limited in its applicability. It is incapable of giving even approximate velocity distribution curves, and has so little resolution as to be probably quite useless in dealing with any velocity of more than a few volts.

For the purpose which the writer had in view, it was necessary to obtain the actual velocity distribution existing among the electrons in the mercury vapor. Therefore, an attempt was made to eliminate, so far as possible, the following obvious defects inherent in the grid type of tube, when used for such a purpose:

1. The electrons enter the retarding region with only one component of their velocities in the direction of the retarding field.
2. Collisions are made in this region, so that the electrons reach the plate only by diffusion. In the work of Sponer the free path was about half a millimeter.
3. Many electrons, though reaching the receiving plate, are reflected.
4. Electrons are reflected with loss of velocity from the grid.

The apparatus as finally developed is shown in Fig. 3. An earlier form of tube was used in taking some of the observations presented in this paper. It was the same in principle, but differed somewhat in design from the final form shown. These differences will be mentioned after describing the tube represented in Fig. 3.

The glass containing tube is shown shaded. *a* represents the cathode, an oxide-coated sheet of thin platinum supported on a small quartz tube and heated from above by a tungsten spiral. This furnishes a

[1] The recurrence of peaks gives, to be sure, evidence concerning the continuity of these collisions at higher velocities but these peaks are usually too complicated to be fully interpretable.

[2] Zeit. d. Phys., 7, p. 185 (1921).

source of constant potential and one which is quite steady. *b* represents a nickel grid and wire cylinder; *c* shows a platinum cap, tightly fitting the inner tube and perforated by a small hole (0.6 mm. in diameter).

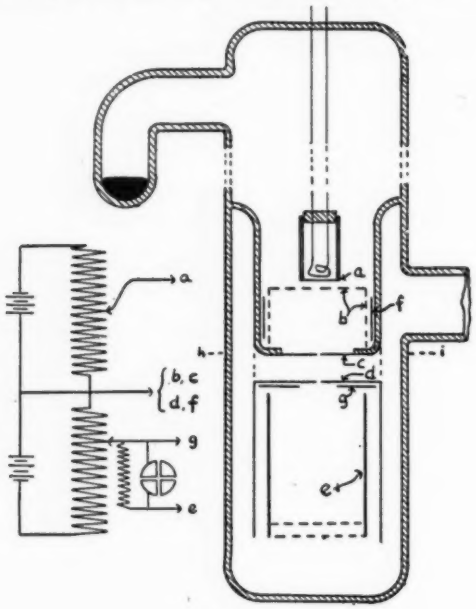


Fig. 3.

A nickel cylinder covered by a platinum disc with a similar perforation is shown at *d*, and *e* shows another nickel cylinder with its lower end covered by two layers of fine meshed nickel gauze and well insulated from other parts of the apparatus. To reduce electronic reflection, the inner walls of this cylinder are also lined with gauze. The distance between *c* and *d* is about 8 mm.

The tube is thus divided into two parts, communicating through the small hole *c*. During an experiment the upper part of the tube is electrically heated to any desired temperature (the mercury in the offset tube being somewhat underheated), and the lower part, below *h–i*, is immersed in liquid air. Under these circumstances, it is possible to maintain a high mercury pressure in the upper region, with a very much lower pressure in the region between *c* and *d*, and a good vacuum within the cylinder *e*. To avoid condensation of mercury on the nickel cylinders, the cylinder *d* was wrapped with nickel wire (not shown), and could be electrically heated while the tube was immersed in liquid air. A cylinder of thin aluminum sheet (not shown) was placed outside the nickel wire to reduce the radiation from the heated wire to the walls of the tube. A platinum cylinder is represented by *f*, placed behind the wire

cylinder *b* and insulated from the hot, semi-conducting walls. This was used to take ionization curves in the usual fashion to check the behavior of the tube. *g* represents a nickel guard ring intended to be used to cut down the reflection of electrons from *e*, which electrons would have otherwise been attracted away from *e* by the field between *e* and *d*. The reflection was in fact small with this tube, and the ring had little effect.

All lettered parts had separate leads to the outside of the tube, but normally *b*, *c*, *d*, and *f* were maintained at the same potential. The electrical connections in such a case are shown in the figure. From *a* to *b* an accelerating field of any desired value is applied. The electrons enter the region below *b* with the velocity corresponding to this difference in potential, and collide with many mercury molecules here; some reach *c* and after a last collision pass through the small hole, and of these some enter the hole in *d*. A variable retarding difference of potential is established between *d* and *e*, and the current to *e* is measured as a function of this potential difference.

The earlier form of tube differed in design from that shown in Fig. 3 in that parts lettered *f* and *g* were missing, and a less direct method of eliminating the mercury vapor from the evacuated region was employed. In this case, instead of freezing the vapor out on the sides of the main tube, short side tubes were used, ending in mercury vapor traps. This tube probably gave a somewhat higher vapor pressure in *e* than did the later form shown.

An extremely small portion of the total current passes the two holes, and it is necessary to measure this current with an electrometer. A constant deflection method was used, using a shunting resistance of some 10,000 megohms of graphite on glass. This was kept dry over phosphorous pentoxide, and was very satisfactory, giving no evidence of polarization.[1]

The electrometer deflections were recorded in most cases photographically. This gave a continuous and rapid record of the current as the retarding potential was gradually increased. A Compton electrometer was used, with a period short enough to enable it to follow the impressed variations quite accurately.

The electrons passing through the perforations will reach the cylinder *e* and be measured as current so long as their velocity is greater than the

[1] In this method there is a slight correction to be made to the apparent potential of *e*, due to the *IR* drop in the shunting resistance, but this was only about 0.2 volt for a maximum deflection, and this correction has not been applied to the curves. Its effect will be appreciable only in estimating the distribution of velocities of emission which is in fact 0.1 or 0.2 volt less than that apparent from the curve.

retarding potential. The ordinate at any point on the current-retarding potential curve represents the number of electrons which had a kinetic energy greater than the retarding potential, or from the slope of the curve the number having any particular velocity is given. It is assumed that the electrons going through the holes are representative of those in the region *b*. If, then, it were possible to produce in this region electrons with kinetic energies of exactly 9 volts, the curve should be quite horizontal from 0 to 9 volts, and suddenly drop to zero. Or if half of these 9-volt electrons made collisions involving an energy loss of 4.9 volts, the curve would have a constant ordinate for retarding potentials from 0 to 4.1 volts, and then suddenly drop to a half value, which it would maintain until 9 volts. This illustrates the strong possibilities of the arrangement in resolving neighboring critical velocities, the resolution being only limited by the range of velocity distribution attainable.

In Fig. 7 the upper curve is a typical velocity distribution curve in vacuum (mercury free), taken with the tube illustrated in Fig. 3. The accelerating potential in this case was 12 volts. This curve shows a very satisfactory performance of the tube and a velocity distribution from the oxide-coated source which is mostly within a volt. The curve remains horizontal to 8 volts, then after a slight increase falls rapidly to zero, the slow electrons being lost in appreciable numbers at about 10 volts (which indicates a contact potential difference between *a* and *e* of 2 volts) and the fastest ones are lost when the potential is raised to 11 volts. The slight maximum at 9.5 volts is probably due to reflection of electrons from *e*. This reflection is less at low velocities, and consequently the number of electrons received and held by *e* is actually greater for high retarding potentials than for lower. There is every reason to believe that the drop in the curve does give very nearly the actual distribution of initial velocities.

CONDITIONS FOR THE OCCURRENCE OF 4.9-VOLT AND 6.7-VOLT COLLISIONS.

Figure 4 represents curves taken with the earlier form of tube. The mercury temperature was 140° C. in the cases of the upper two curves, and for the others 120° C., but the actual vapor pressures in *b* with this tube were somewhat less than the saturation pressures at these temperatures.[1] For each curve the accelerating potential (between *a* and *b*) is a constant, and its value corrected for contact difference between *a* and *b* is given for each curve; the uncorrected value is given in parenthesis.[2]

[1] Owing to condensation on colder walls, which was not entirely avoided in this tube.

[2] The correction for contact difference between *a* and *b* was made by taking the usual resonance curves, measuring the current to *c*. The first peak occurred at 6 volts, instead

The curves were photographed with the current to e (ordinate) as a function of the retarding potential between b and e; in Fig. 4 the different curves have been so placed that the corresponding drops on different curves fall approximately above one another. The abscissa marked o

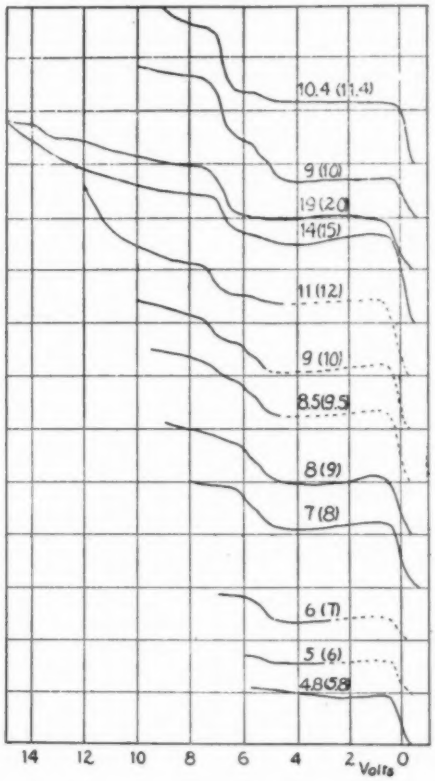


Fig. 4.

represents then for each case the potential of the source, and the other abscissas give the potential of e relative to the source.

However, the meaning of the curves is most easily seen, if the scale of abscissas is for the present ignored and it is remembered that the left-hand end of any curve gives the current to e for no retarding potential between b and e.[1] From here, as we pass to the right, the retarding potential gradually increases, the vertical rulings giving this potential in two-volt intervals. For instance, the curve labeled 6 (7) is for electrons with a corrected velocity as they enter the region between b and c of 6 volts. As we proceed from left to right on this curve, we find the

of 4.9, and ionization at 11.3 instead of 10.4, indicating a correction of one volt to be applied to the observed accelerating potentials.

[1] That is, no apparent potential difference—there is a con.act difference of potential.

current at first decreases slightly until the retarding potential is 1.3 volts, when it drops more rapidly to about half its former value. As the retarding potential is further increased, the current stays nearly constant (increasing slightly) until a retarding potential of 6.5 volts is reached, when it drops rapidly to zero. (The fact that it requires 6.5 volts to stop 6-volt electrons is due to a contact difference in potential between *b* and *e*.) Of the total number of electrons passing through the hole in *d*, we see that we continue to get about half, with retarding potentials as large as 6.5 volts; the other half were lost with a retarding potential some 4.9 volts less than this—this group then had given up 4.9 volts of their initial energy by collision. The energy losses which the electrons have suffered are to be determined then by counting back from the steepest part of the terminal drop at the right end of the curve to similar points on preceding drops. Since the terminal drops come at approximately zero on the scale of abscissas, these energy losses can be read directly from that scale.

The lowest curve was taken with an accelerating potential of 5.8 (corrected 4.8) volts, which had been observed to be just less than the potential at which inelastic collisions set in. It is seen that in general the curve remains horizontal until the retarding potential is enough to overcome the velocity given by the accelerating field—that is, there is here no indication of energy losses due to collisions. The slight drop which occurs at first in the curve and which is found at the beginning of all the curves is probably due to mercury vapor which it was impossible to completely eliminate from *e*. The slight rise which occurs just before the terminal drop has been accounted for as due to electron reflections from *e*. Such a curve gives the best direct evidence that we have of the elasticity of collisions below the resonating potential.

The next curve[1] with 5 (6) volts' accelerating potential was (for the fastest electrons) just above the resonating potential, and gives direct evidence of inelastic collisions involving an energy loss of approximately 4.9 volts. The slight drop at the left end of this curve is due to electrons suffering such collisions. The 6 (7)-volt curve also shows this same energy loss, in this case suffered by a much larger proportion of electrons. At all higher voltages a similar collision is evidenced. Beginning at 7 volts (corrected), however, there are indications of another type of collision with energy loss of 5.7 volts. And at 8.5 volts the expected collisions involving losses of 6.7 volts begin to occur, and become more pronounced at 9 volts. The next three curves are taken above the ioniza-

[1] Since the general shape of the curve was in some regions well known from previous work, and since it was desired to take these curves in as rapid succession as possible, the dashed portions were not actually observed.

tion point, and show the extreme importance of the 6.7-volt type of collision, the 4.9-volt and 5.7-volt drops having nearly disappeared. The 19-volt curve shows indications of an energy loss of 2×6.7 volts, corresponding to two of the more probable collisions.

The upper two curves of Fig. 4 were taken at higher vapor pressures, and show somewhat more pronounced drops at the critical potentials. The upper curve was taken just above the point at which ionization set in, and this shows that, at this voltage the 4.9 types of collision have become extremely improbable.

The 6.7-volt type of collision is then possible, and indeed above the ionization point is extremely probable as compared with the 4.9-volt collision. It does not seem to occur, however, in the cases of electrons with velocities only slightly in excess of 6.7 volts, but first occurs to an appreciable extent at 8.5 volts. The results are in exact accord with the hypothesis set forth earlier in the paper. That hypothesis was there seen to be required to explain the results of Mohler, Foote and Meggers; the present experiment is its direct proof. This completes the case for a 6.7-volt type of collision.

The distribution of velocities is more directly shown if the slope of the curves of Fig. 4 is taken and plotted as a function of the retarding potential. Such curves are given in Fig. 5. As in Fig. 4 the curves are super-

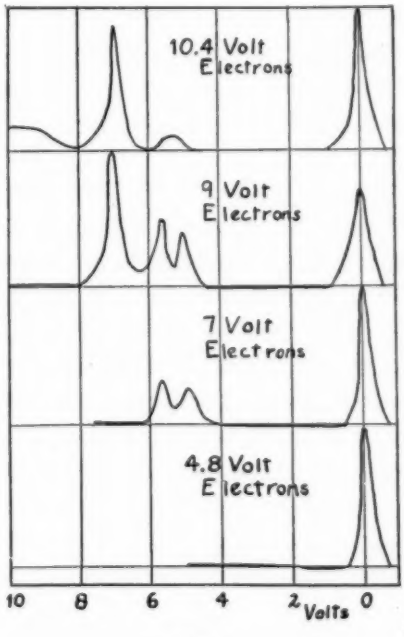


Fig. 5.

imposed and the scale of abscissas, instead of giving the retarding potential, gives directly the energy losses which have been suffered. The curves which are shown are for electrons which before collision had energies of 4.8, 7, 9, and 10.4 volts, respectively. The ordinate gives the relative number of electrons which have suffered energy losses corresponding to any particular value of the abscissa.[1] The negative values of the ordinates are of course meaningless, and are due, as mentioned above, to reflection from the walls of the receiving tube.

COMPARISON WITH SPECTROSCOPIC DATA.

Mohler, Foote and Meggers obtained resonance curves for cadmium, zinc, magnesium, and calcium similar to that for mercury. In each of these cases, then, there are two types of inelastic collision, and in the cases of the first three metals their curves show that the conditions for the two types of inelastic collisions are similar to those which have been shown to exist for mecrury.

Corresponding to these types of inelastic collision, mercury, as is well known, has been found to give a single line spectrum λ 2536, which may be obtained with an impact potential of 5 volts. The line λ 1849 has never been observed below the ionization point, probably due to its strong absorption by the vapor. For three of the other metals both lines have been observed,[2] the line of shorter wave length first appearing in the case of zinc about 0.4 volt, in the case of cadmium about 0.7 volt, and in the case of magnesium 0.6 volt above the corresponding resonance potentials. This is in satisfactory agreement with the discovery of the second type of inelastic impact by Mohler, Foote and Meggers, and with the present investigation.

McLennan and Ireton have maintained that while the λ 2536 line is the more easily obtained by electronic bombardment, the series whose first member is λ 1849 is probably the one which corresponds to some very simple type of electronic vibration within the atom, and is more fundamental in character. This view is in accord with the present results which show that though the longer wave length is more readily excited at low voltages, at higher voltages it becomes quite insignificant in comparison with the radiation of the second type.

The results of Davis and Goucher, who found indications of strong photoelectric emission at 6.7 volts, and the more recent results of Franck

[1] While too much weight must not be laid upon the exact values of the ordinates the area under the peaks give the number of electrons which have suffered the corresponding energy losses.

[2] McLennan & Ireton, Phil. Mag., 36, p. 461 (1918); McLennan, Proc. Roy. Soc. A., 92, p. 574 (1916); Mohler, Foote & Meggers, Jour. Opt. Soc., 4, p. 364 (1920).

and Einsporn, who also detected this line among others, are not to be cleared up in this fashion. The methods employed by these writers gave the potentials at which the photoelectric emissions suddenly increased in value, and would be quite unable to detect the 6.7 type of emission if it did not begin until 8.5 volts.

In Goucher's curves we find a photoelectric effect beginning at 4.9 volts, which increases several fold between 6 and 7 volts, and a second quite sudden increase in the current at 9.8 volts. Perhaps these curves are not to be quantitatively explained. It is certainly difficult to see why, if the larger part of the photoelectric current just below 9.8 volts was due to 6.7-volt collisions, as the curves are interpreted to mean, so large an increase in current takes place at 9.8 volts which corresponds to two collisions of the 4.9-volt type.

Franck and Einsporn find curves having the same general shape as those of Davis and Goucher, but with large numbers of discontinuities in shape. These discontinuities, interpreted as spectrum lines, agree wonderfully well with prominent mercury lines. These lines have never been spectroscopically observed under these conditions. There are several difficulties which are met when we try to account for the shape of this curve, and the lack of proportionality between the magnitude of the photoelectric effect and the probability of inelastic impact is hard to explain—yet the checks found with spectral data are so striking as to make it almost impossible to doubt the interpretation. There remains, however, much to be done in correlating spectroscopic, photoelectric, and inelastic impact data, and it is not strange if the present experiment does not seem compatible with the photoelectric data.

Other Inelastic Potentials.

Two features of the present type of tube seemed to make it admirably fitted to detect other forms of inelastic collisions than those of the 4.9- and 6.7-volt type.

In the first place, the resolving power of this arrangement should be greater than of that hitherto employed. In the usual form of curve, the suddenness of the drop at a critical potential largely depends upon what function the probability of inelastic collisions is of the velocity. These collisions do not take place immediately as the critical potential is reached, but in increasing numbers as it is exceeded. This has just been shown to be strikingly true in the case of 6.7-volt collisions and for a considerable range of voltage seems true for the collisions at 4.9 volts. And equally serious is the fact that the recovery from such potential is not immediate but distorts the curve seriously for several volts after the potential has been passed.

The resolving power of the present arrangement, on the other hand, is conditioned only by the velocity distribution of the source. The accelerating potential may be placed at a value which will give the maximum number of collisions of the type desired, and the retarding potential will detect the number of such collisions present, the drop being completed in a range equal to the initial distribution. This distribution is, it is true, a serious matter, but it is hoped that this can be cut down to a small fraction of its present value.

In the second place, such a tube integrates the effects of the different types of collision, and so even though the initial potentials were too close to be observed separately, the presence of such potentials would be indicated by a gradual drop in the curve in that region. Assuming a perfect tube, the curve will be horizontal, except at such potentials.

It has already been seen that an inelastic collision appears to take place, involving an energy loss of about 5.7 volts. There is little evidence of still other types of inelastic collision. The region about 6.7 volts has been investigated with some care but no consistent inflections were found which could be attributed to other lines. The gradual downward slope of the curve in this region probably should be attributed to the imperfections of the method, and probably to the presence of mercury vapor in the supposedly evacuated region.

The drop at 5.7 volts is too pronounced to be disregarded, and to some extent supports the conclusions of Franck and Einsporn, who, it has been remarked, found strong indications of spectral lines and weaker evidence of inelastic collisions at 5.45 and 5.7 volts.

Turning again to spectroscopic observations, it will be recalled that the lines λ 2536 and λ 1849, corresponding to 4.9 and 6.7 volts' impact velocity, have been found to be absorption lines as was to be expected from the theory. A group of absorption lines has also been observed in the neighborhood of 2330, and also a line at 2140 Ångstroms.[1] No absorption lines other than these have been observed by McLennan and Edwards above 1849 Ångstroms. These wave lengths correspond to electron energies of 5.3 and 5.9 volts, respectively, and agree with the present observation of an energy loss in the neighborhood of 5.7 volts.

Collateral evidence for the existence of an inelastic collision in this neighborhood is furnished by resonance potential curves obtained by the writer some time ago, and which at that time were quite inexplicable, as in many features they still are. These curves (Fig. 6) resemble in many details one published by Mohler, Foote and Meggers. The peak

[1] Wood & Guthrie, Astro. Journ., 29, p. 211 (1909); McLennan & Edwards, Phil. Mag., 30, p. 295 (1915). McLennan & Edwards failed to find an absorption line at 2140, but it is not clear that this was not due to experimental difficulties.

appearing at 9 volts corresopnds to one which they attributed tentatively to λ 1435.6 or λ 1402.7. Interestingly enough, this curve shows a pronounced maximum at 5.8 volts, which may be supposed to correspond to that placed at 5.7 volts from the velocity distribution curves.

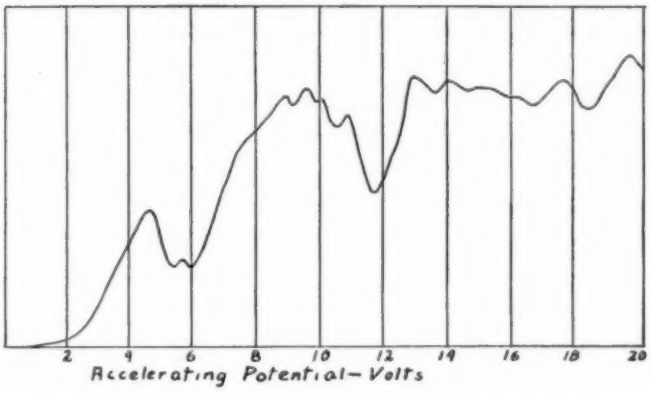


Fig. 6.

IONIZATION.

In contradiction to the generally accepted belief concerning the phenomena taking place at the ionization point, the curves of Fig. 4 give no indication of a loss of 10.4 volts of energy. No evidence for such a loss exists elsewhere.[1] The 10.4-volt inflection in the usual form of ionization curve which indicates ionization, does not reoccur at 20.8 volts, and it has been suggested elsewhere that this may mean that ionization does not involve a loss of a definite amount of energy in the same manner that a resonating collision does. The absence of the inflection at 20.8 volts cannot be considered conclusive evidence in the matter, however, as the experimental conditions make it quite likely that the double collisions necessary to give this inflection would be very improbable, and if occurring be difficult to detect.

It would be quite in accord with the Bohr theory if energy was absorbed above the ionization point in any amount above that just required for ionization. As long as the excited electron stays attached to the atom, its energy absorption is definitely fixed by the energy of an initial and a final position. But a free electron may have any velocity, and so it is quite in line with the theory that a 19-volt electron, say, should lose any part or all of its energy; if it lost all of its energy, the emitted electron would have $19 - 10.4 = 8.6$ volts of energy after emission, and this

[1] Except some recent results, as yet unpublished, of Noyes and Gibson, which seem to indicate that such a loss does occur.

effect would be indistinguishable from the case in which the primary electron lost 10.4 volts and the secondary electron had zero velocity; if it loses energy in any random amount over 10.4 volts, the emitted electron must, by this accepted theory, have enough to make the sum of the two remanent energies 8.6 volts. The first case leads us to expect a sudden drop in the curve at 10.4 volts from the terminus, and another at zero retarding potential. The second case would be shown by a curve which gradually drops in the region from zero to 8.6 volts retarding potentials, and at 8.6 volts (with a perfect tube) becomes horizontal, or at least has a change in slope at this point. Neither is in accord with the results of this experiment. It is true that, though the curves do not have the change in slope we should expect at the ionizing point on the curves, they do have a continued drop, which has been accounted for by the presence of mercury in the region from *c* to *e*. It is possible that this is rather the effect for which we are looking, the drop being continued below the ionizing point by a miscellany of critical potentials in that region which have not been resolved.

To test this very important point, another tube was designed with a view to more immediate removal of the mercury which passes through the holes, to eliminate as far as possible the reflection of electrons, and to make it possible to check the behavior of the tube by taking conventional ionization curves. This is the tube which has been described (Fig. 3). The observations discussed in the above sections have all been checked with this tube.

It has been possible, under suitable conditions, with this tube to obtain curves which were practically horizontal except at the critical potentials. The upper curve of Fig. 7 is a typical velocity distribution

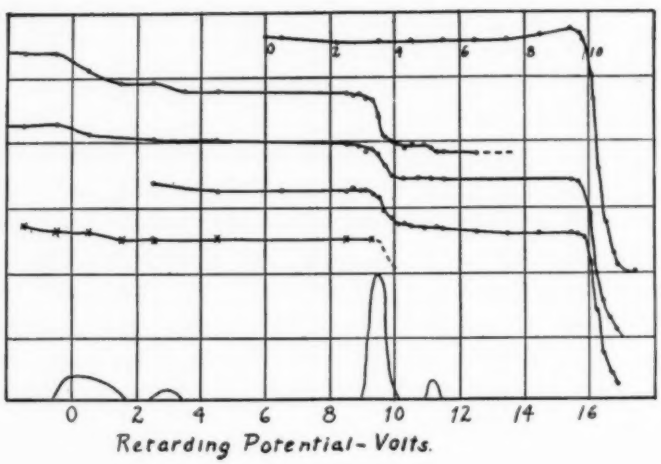


Fig. 7.

curve in vacuum. The other curves are for 16.5-volt electrons with the mercury at 90°. The cylinders *d* and *e* had been heated for some hours to drive out mercury as far as possible; during the observations they were cold.

By taking ionization curves by the usual method, measuring the current to *f*, it was ascertained that strong ionization was taking place under these conditions.

Several curves were taken with a view to detecting energy losses greater than 6.7 volts and these are given in the figure, with the current plotted against the retarding potential. From one of these curves (the upper one) the slopes have been taken and the lowest curve of the figure shows these slopes plotted as a function of the retarding potential. The curves all drop during the first volt; and two of the curves show another slight drop at about 3 volts. The current then remains constant until a retarding potential of about 9 volts is reached, when a drop occurs which is due to electrons which have made a 6.7-volt collision. A much smaller drop occurs at 11 volts, attributable to collisions of the 4.9-volt type. The drop which occurs in two of the curves at about 3 volts can be accounted for as due to two collisions of the 6.7-volt type. Between 3 and 9 volts the curves show no decrease in the current with increasing retarding potential and so are in contradiction both with the view that a loss of exactly 10.4 volts occurs at ionization and that a loss of energy in random amounts above this value can occur, with a transfer of the excess over that needed for ionization to the secondary electron. The first view would lead us to expect a sudden drop in the curve between 5.5 and 6.5 volts; from the second we would expect a gradual decrease in current in the region from 0 to 6 volts' retarding potential.

On all of the curves a slight drop is to be observed with small retarding potentials (1 volt) and the same effect is seen in curve 11 (12) of Fig. 4. This indicates a number of very slow electrons present after collision. It is not to be expected that these current drops will be large, because the slow electrons which are here being measured will quite likely combine with the positive ions present before they reach the hole in *c*. However, if *c*, *d*, and *e* are given a slight accelerating potential with respect to *b* ($\frac{1}{4}$ volt), we should expect to get more of them, and in fact it is observed that under these conditions the current to *e* is greatly increased, perhaps twenty-fold. The current is reduced to its normal value, unless *e* is slightly accelerating. Such a phenomenon is only to be observed with accelerating potentials sufficient for ionization. This shows that there are indeed present at ionization a large number of electrons with zero velocity. Whether such electrons are the primary ones from the cathode,

or those released at ionization, cannot be directly determined. However, since Fig. 7 shows that a total loss is the only loss greater than 6.7 volts which occurs, we may suppose that both primary and secondary electrons are represented in this group; that is, that after an ionizing collision, both primary and secondary electrons have zero velocity.

This conclusion seems to disagree with the Bohr theory, but perhaps this disagreement is not insuperable. Immediately after the removal of an electron from the atom it is conceivable that the remaining electrons do not have stable configurations and are quite easily displaced. Possibly after the electron strikes the atom and removes one electron, it may use its remaining energy in displacing other electrons in the now less stable ion. If the conclusion drawn from the experiment is to be accepted as valid, by some such picture as this it is possible to remove the discord with the Bohr theory.

Professor Wood [1] has found that above the limit of the principal series, the light absorption of a vapor becomes continuous. Such light should produce ionization, and this has indeed been shown to be the case in an investigation which has just been completed by R. C. Williamson. This continuous absorption of light for frequencies greater than the limit of the principal series presents an obvious parallel to the continuous absorption of energy of the electron when its energy is above the ionizing potential. It is a very interesting question whether the emitted electron in this photoelectric ionization has an energy at emission corresponding through the $h\nu$ relation to the amount by which the frequency of absorbed light exceeds the limiting frequency of the principal series. Such has been our general view, but if the parallel with the present results is perfect, these emitted electrons should have a zero velocity.

CONCLUSIONS.

The principal results which have been obtained from an examination of the residual energies after collisions of electrons in mercury vapor are:

1. The discovery by Mohler, Foote and Meggers of a resonance potential involving an energy loss of 6.7 volts has been confirmed. It has been shown that while this collision does not occur below 8.5 volts, at voltages above the ionizing point, this type of collision attains overwhelming importance in comparison with the collisions of the 4.9-volt type.

2. It is probable that inelastic collisions involving an energy loss of about 5.7 volts also occur, checking, to this extent, with the conclusions of Franck and Einsporn. The absorption lines which have been found

[1] Phil. Mag., 18, p. 531 (1909).

in the spectrum of mercury support this view. Inelastic collisions corresponding to the other photoelectric lines of Franck and Einsporn have not been found.

3. At ionization the electron loses its total energy, even though this much exceeds the ionizing potential. The electron which is the product of the ionization seems likewise to have a negligible energy.

UNIVERSITY OF WISCONSIN.

ELECTRICAL CONDUCTION ACROSS MINUTE AIR-GAPS.

By James W. Broxon.

Synopsis.

Electrical Conduction across Minute Air-gaps.—As some results obtained by R. W. Wood are at variance with those of other observers, further experiments seemed desirable in which the separation of the metallic electrodes was determined optically. Therefore, two optical surfaces of nearly the same curvature were made conducting by depositing gold upon them by cathode discharge and were supported so as to be nearly in contact. Then, as the upper one was semi-transparent, the distance apart was determined by the interference rings produced by light of wave-length 0.546 μ. Using voltages of from 1.5 to 60, the minimum distance at which no conduction took place and the maximum distance at which conduction occurred were observed. Both these distances varied from less than a wave-length to several wave-lengths. In some cases the resistance of the gap during conduction was measured; it was found to obey Ohm's law and to be unaffected by radiation from 3 mg. of radium. The results suggest that the conduction was due to small projections from the electrodes or to dust particles. No disruptive discharge took place even when the potential gradient rose to 640,000 volts/cm., probably because the potential was less than the minimum which previous researches had indicated is necessary.

Existence of electron atmospheres at metallic surfaces, which was suggested by R. W. Wood to explain his experiments, seems very doubtful in view of the above results. At any rate, the atmosphere cannot extend more than one fourth wave-length or 0.14 μ beyond the molecular surfaces of the gold electrodes.

SOME time ago R. W. Wood [1] performed experiments which provided strong evidence of the existence of a medium, presumably an atmosphere of free electrons, capable of carrying electric currents between differences of potential of the order of one volt and extending beyond the molecular surface of a metal through a distance as great as thirty wave-lengths of sodium light. Not only were these results at variance with those of previous experimenters with small gaps (Carr,[2] Shaw,[3] Almy,[4] Williams,[5] etc. . . .) who found evidence that as a gap in an electric circuit is made very small there exists a minimum potential of the order of 350 volts which can cause a current to flow without actual contact, but Brown,[6] Englund,[7] and Householder[8] have since

[1] Phil. Mag. (6), 24, p. 316, 1912; R. W. Wood.
[2] Proc. Roy. Soc., LXXI., p. 374, 1903; W. R. Carr.
[3] Proc. Roy. Soc., LXXIII., p. 337, 1904; P. E. Shaw.
[4] Phil. Mag. (6), 16, p. 456, 1908; J. E. Almy.
[5] Phys. Rev., 31, p. 216, 1910; E. H. Williams.
[6] Phys. Rev. (2), 2, p. 314, 1913; F. C. Brown.
[7] Phil. Mag. (6), 27, p. 457, 1914; C. R. Englund.
[8] Phys. Rev. (2), 4, p. 47, 1914; F. F. Householder.

performed experiments dealing directly with the question and have secured negative results. It is important to observe, however, that in practically every instance the point of actual molecular contact (if one may say that) was established by electrical means, thus eliminating the true field of experimentation, for by this means it could only be determined that a continuous circuit, perhaps partially composed of an atmosphere of free electrons, had been established. This objection can not be offered against the work of Brown and Householder, but in the one case perfect insulation could not be obtained across a gap of less than nine wave-lengths, and in the other the actual areas of the opposed electrodes were exceedingly small, and no statement was made concerning the precautions taken to insure conductivity at all parts of the circuit other than the one under investigation.

Because of these considerations, it was suggested by Dr. W. F. G. Swann that the problem be investigated by a method which should reproduce as nearly as possible the conditions under which Wood found the effect most noticeable and which should at the same time eliminate difficulties involved in other methods used. The writer was able to do this in the following manner:

Care was taken to select a double-convex and a double-concave lens such that a very regular series of Newton's rings could be secured at whatever place the lenses were brought into contact. After a heavier ring had been deposited about its edge, one surface of each lens was then completely covered with a deposit of gold thrown down in a vacuum. A concave surface, of about 206 cm. radius of curvature and 3 cm. diameter, was covered with a film rather heavier than that known as semi-transparent, while a convex surface of about 127.5 cm. radius of curvature and 5 cm. diameter was covered with a film which was quite transparent.

A partial cross-sectional diagram of the apparatus made to hold the electrodes and to adjust the extent of their separation is shown in Fig. 1. The base of the instrument consisted of two brass rings about 4 mm. thick and with external diameters of 10 cm., held rigidly separated at a distance of 2.5 cm. by stout brass rods. The upper surface of the second ring was made with a raised collar about its inner circumference, the top of this being cut down until the remaining ledge supported the concave lens with its gilded surface well above any portion of the ring. At one place an incision was made in the collar to enable a small clamp, fastened to the lower side of the second ring and extending up along the cylindrical side of the lens, to hold a small piece of tin foil tightly against that side without exposing any metal at an altitude as great as that of the upper surface of the lens.

The convex lens was held similarly in a third ring with its gilded surface down, the diameter of the lens being sufficiently large that its supporting clamps were further separated from the second ring than was the upper

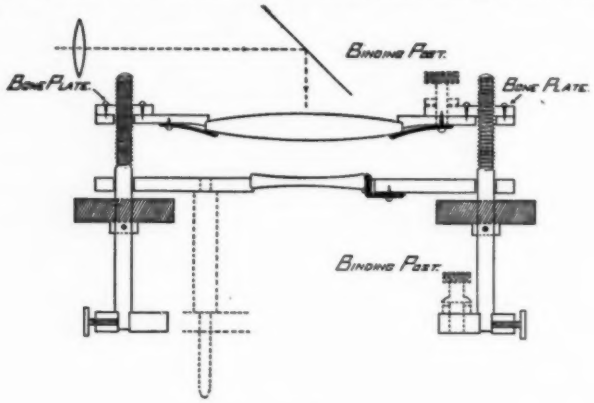


Fig. 1.

film from the lower. The third ring was supported above and insulated from the rest of the instrument by brass rods which turned freely in the base and passed through threaded bone plates fastened to the ring. Adjustments were made either by heating the rods last mentioned or by turning them. While backlash was largely eliminated by insulated spiral springs, there was still sufficient freedom to enable the films to be brought into contact at any point desired.

By means of a small plate of glass placed in a frame at an angle of 45 degrees to the planes of the rings, the green light from a mercury arc lamp was reflected against the lenses so that a system of Newton's rings was formed by reflection from the two gold films. In effect, then, two sections of very smooth thin spherical gold shells could be made to approach each other in a uniform manner. The center of the system of rings formed was observed through a traveling microscope between parallel hairs. Metallic contact was taken as occurring when the center of the system remained light and spread out over the field when greater pressure was exerted upon the lenses. As the thumbscrews were turned in a direction which would separate the films, each change in the center of the system from light to dark or from dark to light indicated an increase of one fourth wave-length between the points on the films nearest contact. The monochromatic filtered line used was .546 μ. Future reference to "wave-length" will be taken as indicating this distance.

The apparatus holding the films was first connected as the unknown resistance in a Wheatstone net with a very sensitive galvanometer, and

the resistance of the gap was measured as its magnitude was varied. Observations made when true metallic contact had been made certain in the manner described showed the resistance to be quite constant under such conditions, varying only as points of contact between the films varied in their distance from the conducting clamps. Observations of the resistance of the gap were then made, usually at every quarter wave-length increase in the shortest distance between the films. Readings secured in this manner are given in Tables VII., VIII., IX., and X. The potential applied was 1.4 volts, supplied by one dry cell. Infinite resistance in these tables is taken to mean that the resistance was greater than 9,000,000 ohms.

Tables.

In the following tables a row labelled (*A*) contains the values of the magnitudes in wave-lengths of the gaps at which conduction ceased, while one labelled (*B*) indicates the corresponding values for the re-sumption of conduction.

Table I.

(*A*) $2\frac{1}{2}$, 1, 10, $2\frac{1}{2}$, $2\frac{3}{4}$, $13\frac{1}{2}$, $3\frac{3}{4}$, $1\frac{1}{2}$, $3\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, $1\frac{1}{2}$, 3, $2\frac{1}{2}$, $3\frac{1}{2}$, $3\frac{3}{4}$.

Table II.

(*A*) $1\frac{1}{2}$, $3\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, $1\frac{1}{2}$, 3, $2\frac{1}{2}$, $3\frac{1}{2}$, 2 , 7, $3\frac{3}{4}$, $9\frac{1}{2}$, 6, $3\frac{1}{2}$, 8, 2 , $6\frac{1}{2}$, $1\frac{1}{2}$, $1\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, $4\frac{1}{4}$, 2 , 2 .
(*B*) $1\frac{1}{2}$, 4, $7\frac{1}{2}$, $3\frac{1}{2}$, 2, $1\frac{1}{2}$, $1\frac{1}{2}$, $1\frac{1}{2}$, $1\frac{1}{4}$, 1 , $1\frac{3}{4}$, 2 , $1\frac{1}{2}$, $1\frac{3}{4}$.

Table III.

(*A*) $1\frac{1}{2}$, $2\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$, 1, 1, $1\frac{1}{2}$, $3\frac{1}{2}$, $5\frac{1}{4}$, $3\frac{1}{2}$, $2\frac{1}{2}$.
(*B*) $\frac{5}{8}$, $\frac{1}{2}$, 1, $1\frac{1}{4}$, $2\frac{3}{4}$, $4\frac{3}{4}$, $3\frac{1}{8}$, .

Table IV.

(*A*) 3, 2, 2 , 3 , 2 , 3 , 2, 2 , $1\frac{1}{2}$, 2–.
(*B*) 2, 1, $1\frac{1}{4}$, $2\frac{1}{2}$, $1\frac{1}{4}$, $1\frac{1}{2}$, 1, $1\frac{1}{2}$, 1 , $1\frac{1}{4}$.

Table V.

Volts.	Amperes.	Ohms.
.06	.00066	91
.07	.00070	100
.10	.00060	166
.155	.00086	174
.20	.00120	166
.175	.00105	157
.22	.00130	170
.23	.00135	170
.24	.00140	170
.25	.00170	150
1.238	.00820	150
1.345	.00840	160

TABLE VI.

In row (*C*) of this table are given the magnitudes in wave-lengths of the gaps across which the higher voltage discharges occurred.

(For Preliminary Potential Differences.)

(Volts) 3 , 3 , 4 , 4 , 3 , $4\frac{3}{4}$, $3\frac{3}{4}$, $3\frac{1}{2}$, $2\frac{3}{4}$, $3\frac{1}{4}$, 3 , 3 , $3\frac{1}{4}$, $3\frac{1}{2}$, 3, 3 , 3 , 4 .

(*A*) $1\frac{1}{2}$, $4\frac{1}{2}$, $2\frac{1}{2}$, 3 , $1\frac{1}{2}$, 2 , 2 , $1\frac{1}{4}$, 2 , $2\frac{1}{2}$, $1\frac{1}{2}$, 4 , $2\frac{1}{2}$, $1\frac{1}{2}$, 2, 2 , 2 , $3\frac{1}{2}$.

(*B*) , 2 , $\frac{1}{2}$, $1\frac{1}{2}$, $1\frac{1}{4}$, $1\frac{1}{2}$, 1 , $\frac{1}{2}$, $1\frac{1}{2}$, $1\frac{1}{4}$, 1 , $2\frac{1}{2}$, $1\frac{1}{2}$, 1 , 1, $1\frac{1}{2}$, $1\frac{1}{2}$, $1\frac{1}{2}$.

(For Higher Potential Differences.)

(Volts) 40, 23, 30, 40, 31, 40, 38, 60, 64, 27, 70, 60, 53, 36, 36, 25, 15, 67.

(*C*) $2\frac{1}{2}$, 2, $3\frac{1}{2}$, $1\frac{3}{4}$, 2, $1\frac{1}{4}$, $4\frac{1}{2}$, 2, $1\frac{1}{2}$, $2\frac{3}{4}$, 3, $2\frac{1}{2}$, $1\frac{1}{4}$, 1, $1\frac{1}{2}$, $1\frac{1}{2}$, $5\frac{1}{2}$.

In Tables VII., VIII., IX., and X., row (*D*) gives the magnitude of the gap in wave-lengths, while row (*E*) gives the respective resistances in ohms.

TABLE VII.

(*D*) 0 , $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, 1, $1\frac{1}{4}$, $1\frac{1}{2}$, $1\frac{3}{4}$, 2, $2\frac{1}{4}$, $2\frac{1}{2}$.

(*E*) 8–, 8, 9, $9\frac{1}{3}$, $9\frac{1}{2}$, 10, 11, 13, 15, 50, inf.

TABLE VIII.

(*D*) 0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, $1\frac{1}{2}$.

(*E*) 13.4; 23.6; 29.4; 31.8; inf.

TABLE IX.

(*D*) 0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, 1, $1\frac{1}{4}$, $1\frac{1}{2}$.

(*E*) 19; 45.7; 65.5; 200; 40,000; 3,000,000; inf.

TABLE X.

(*D*) 0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, 1, $1\frac{1}{4}$, $1\frac{1}{2}$, $1\frac{3}{4}$, 2, $2\frac{1}{4}$, $2\frac{1}{2}$, $3\frac{1}{2}$, 4,

(*E*) 16.4; 19.6; 21; 23.1; 25.2; 28.8; 31.7; 34.7; 37; 37.5; 45.8; 4,600; 9,999;

* * * * * * * * *

(Continued.)

(*D*) $4\frac{1}{2}$, 5, $5\frac{1}{2}$, 6, $6\frac{1}{2}$, 7, $8\frac{1}{4}$, $8\frac{1}{2}$, $9\frac{1}{2}$.

(*E*) 14,100; 20,000; 33,000; 160,000; 250,000; 450,000; 1,200,000; 3,200,000; inf.

With certain films, conduction continued in some cases until the films had been separated more than 50 wave-lengths. The magnitude of the distance of separation of the electrodes for cessation of conduction varied greatly with the points on the electrodes nearest contact, but it was impossible to bring some films within three wave-lengths of each other without conduction. It was only after repeated trials with the making of the deposits and with particular care to keep the films at all times protected from dust particles that films were secured which could be brought very nearly together without conduction.

In order to obtain an indication of the nature of the medium providing conduction across the gaps, a test of Ohm's law was made for a constant gap of about $2\frac{3}{4}$ wave-lengths at which there was a considerable resistance. The electrodes were connected in series with a milliammeter, and various

voltages applied, the potentials being determined by a voltmeter constantly shunted across the gap. The results are given in Table V.

For the same reason, the electrodes were left separated by a constant gap whose resistance was about 25.5 ohms, and 3 milligrams of radium contained in a lead case with a small slit were brought from a distant room to a position very near the electrodes. No change could be observed in the resistance of the gap.

It should be noted that the question of chief significance is not across how large an apparent gap conduction could be observed, but how nearly the electrodes could be made to approach without conduction. Since the films were observed to be continuous over the whole opposed surfaces of the lenses, and since considerable areas were separated by practically the same minimum distances, if any one spot could be found at which the electrodes could be brought within two wave-lengths of each other without conduction, and if it were certain that the remainder of the circuit were complete at the same time, this one observation would be sufficient to show that there could not be a general and uniform atmosphere of free electrons extending more than one wave-length above each metal surface, and conduction across apparently greater gaps at other places could be explained by a probable roughness of the surfaces.

Because of this consideration, observations were made of the magnitude of the gaps necessary for no conduction, without finding the values of the resistance during the intermediate steps. The films were first brought into contact and conduction assured. Then they were gradually separated and the point noted at which conduction ceased. Causing the electrodes to approach in such a manner that the point nearest contact should remain as nearly as possible the same throughout the observation, the films were next made slowly to approach each other, and the magnitude of the gap at which conduction was resumed was noted. Such observations were made at various places over the areas of the films. Readings secured in this manner are given in Tables I., II., and III. In each the potential difference applied was 1.4 volts, with the exception of the last ten readings in Table II., which were taken with 2.8 volts.

As a check, similar observations were made in a different manner. The electrodes, one dry cell, and the sensitive galvanometer were connected in series, and the positions for no conduction were taken as those positions at which no deflection of the galvanometer could be observed when the circuit was closed. It should be noted that before or after each reading conduction was secured by bringing the films into contact, thus making sure that the lack of conduction was not due to a break in any other portion of the circuit. Readings secured in this way are given in Table IV.

It was next decided to find just how large potential differences must be applied in order to break down the resistance of the very short gaps which proved insulators for small voltages. A rheostat of considerable resistance was connected directly in a D.C. circuit. Between one end of this and the sliding contact were shunted the electrodes, a resistance of 62,000 ohms, and the galvanometer, all in series. A voltmeter was left permanently shunted across the same two points. The films were first brought together and conduction established with very low voltages. They were then slowly separated and the positions at which conduction ceased were noted, after which they were brought together with the same voltage and the positions at which conduction was resumed were determined. When a spot had been found in this way where the electrodes could be made to approach very closely without conduction with low voltages, they were separated to a distance just greater than that at which conduction with low voltages was known to occur, and the magnitude of the gap kept constant. The applied voltage was then very slowly increased. It was found that as the potential was increased the electrostatic attraction between the electrodes became so great that they were drawn together, but by observing the rings the distance of separation at any instant could be discerned. By waxing a weight to the lower surface of the lower lens, and by slowly turning the thumbscrews in a direction tending to separate the electrodes as the potentials were increased, the magnitude of the gap could be kept quite constant. Since this magnitude could be continuously observed, the electrodes were sometimes separated by a distance greater than that at which it was desired to test the discharge potential, and then allowed to drift down to that distance, the extent of the gap across which conduction first occurred being noted in each case. Although conduction was understood to have taken place whenever the galvanometer began to be deflected, tiny clicking sounds could sometimes be distinguished when the gap was considerably greater than that across which general conduction occurred.

From the readings given in Tables I., II., III., IV., and VI., it is seen that with applied potentials of the order of a volt, it was possible to bring the electrodes so close together that their nearest points were separated by a gap of one half wave-length before conduction took place. This shows that at these points, and necessarily over a considerable area surrounding them, no medium conducting at such potential differences could have extended farther than one fourth wave-length beyond the metallic surface of each electrode.

It should be noted that when conduction was first established by

bringing the electrodes into contact, after which they were slowly separated, conduction persisted in most cases across a much larger gap than that at which conduction was resumed, although great care was taken that the point nearest contact during the approach should be the same as that during the separation. Such a lag might be explained by the presence of long dust particles which would adhere to the two surfaces as they were being separated but which, after the circuit had been broken, would fall down so that the upper lens must descend much lower before reëstablishing contact. Or we might suppose that the particles were distended due to the electrostatic forces acting upon them. It would be difficult to conceive of such a pronounced effect with a uniformly distributed medium.

When the magnitude of a gap was left constant and the current measured for various potential differences, the ratio of the potential difference to the current was, as shown in Table V., as nearly constant as might be expected in the case of a metallic conductor, if one considers the possibility of vibrations of the electrodes and the accuracy with which the ammeter and voltmeter could be read.

Tables VII., VIII., IX., and X. were included as representative of the manner in which the low voltage conductance varied with the magnitude of the gap. If the relative variation be represented by curves, it will be seen (from those representing the data in VII. and VIII.) that the conductivity may vary in a random manner with the extent of the gap. Those for IX. and X., however, have a considerable regularity and the curve (Fig. 2) drawn from the data in X., in which the logarithm of the resistance is plotted against the magnitude of the gap, shows that there were three distinct phases in the variation of the conductivity in this particular case. If the conduction here is to be explained in terms of electron atmospheres, it would seem that we must grant them the privilege of existing in three distinct layers.

It would be much more natural to conclude that the conduction was due to dust particles of different dimensions.

It may be noted that in the case of reading no. (15), Table VI., the potential gradient for discharge if we consider the gap to be the distance between the reflecting surfaces of the films, was about 640,000 volts/cm., while if we consider the gap to be merely the increase over the largest which provided conduction at low potentials, the gradient was practically infinite. When compared with the 30,000 volts/cm. required for discharge across large air-gaps, this seems significant in its relation to the minimum discharge potential theory.

Because of the fact that the two electrodes could be brought within

a distance of from one to one half wave-length from each other without conduction with applied potential differences as high as 36 volts, it seems that a uniform atmosphere of free electrons conducting for low voltages

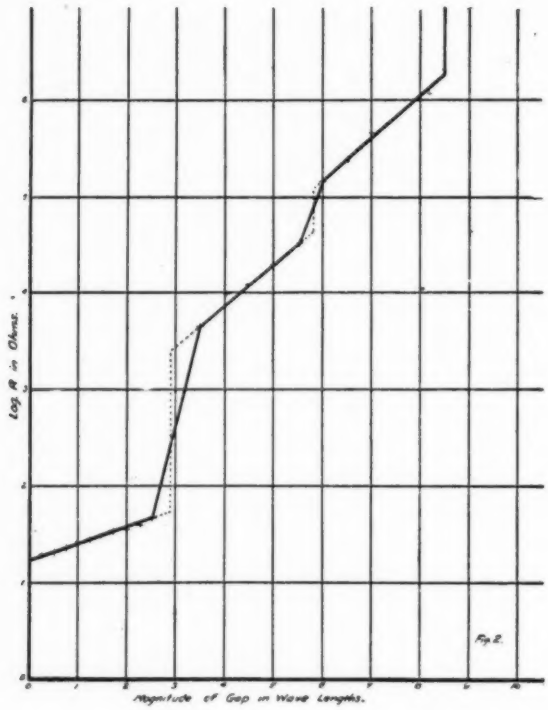


Fig. 2.

can not extend more than half that distance beyond the true metallic surface of a gold electrode.

Because of the fact that Ohm's law held for a considerable gap, because the proximity of radium produced no effect upon the conductance of the gap, because conduction persisted over a longer gap upon separation than that across which it was resumed when the electrodes were brought together, because electrodes could be brought nearer contact without conduction when particular care was taken to keep them entirely free from dust, because of the tiny clicks heard during the operations made in securing the data for Table VI. before general conduction was observed, and because of the peculiar forms of the curves showing the relations between the magnitudes of the gaps and their resistances, the writer feels confident that the conduction across the gaps as observed was due to small metal projections or to dust particles, rather than to a uniformly distributed medium.

The data showing the value of the voltages necessary for electrical discharges serving as insulators for small differences of potential, indicates that a minimum potential may be required to force an electrical discharge across small air gaps, or at least that the potential gradient required is much greater than that required across larger gaps.

The writer wishes to thank Professor W. F. G. Swann for the very kind advice and encouragement which he extended throughout the course of this work.

Department of Physics,
University of Minnesota,
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THE EFFECT OF CERTAIN DISSOLVED SUBSTANCES ON THE INFRA-RED ABSORPTION OF WATER.

BY J. R. COLLINS.

SYNOPSIS.

Infra-red absorption spectra of aqueous solutions of sixteen inorganic compounds from 0.8 to 2.3 μ, have been determined to see how the dissolved substances affect the absorption of the water. Care was taken to eliminate stray light by using two constant deviation glass spectroscopes in series. Readings were taken alternately with a cell containing a solution and with one containing water. Curves were thus obtained for the *alkali hydroxides, five chlorides (Al, Ca, Mg, Na, Sr), five nitrates (Ag, Al, Mg, NH_4, Zn) and three sulphates (Ag, Na, Zn)*. (Figs. 3–16). All solutes decreased the absorption in the water band at 1.44 μ and probably also in the band at 2 μ, whereas all excepting $Al_2(SO_4)_3$, $ZnSO_4$ and the hydroxides increased the absorption in the bands at 0.97 and 1.2 μ. These results do not agree with the solvate theory which ascribes the effect to the formation of hydrates, since some non-hydrating compounds decreased the absorption at 1.44 μ.

Absorption of water, from 0.8 to 2.3 μ, was measured by using cells of different known thicknesses. *The wave-lengths of maximum absorption* were found to be 0.97, 1.20, 1.44, and 2.00 μ, and the corresponding *coefficients* came out 0.448, 1.220, 29.4, and 103, respectively. Such difference as there is between these results and those previously obtained may be due to elimination of stray light. The fact that in the absorption spectrum of water vapor the bands at 1.44 and 2 μ are stronger and the other two bands weaker than for liquid water suggests that the former two bands are associated with a different kind of molecule than the latter two bands. If so, the effect of a dissolved substance on absorption may be due to a change in the relative number of these kinds of molecules produced by the presence of the substance.

INTRODUCTION.

IN their study of infra-red absorption spectra of aqueous solutions, Guy, Schaeffer, and Jones[1] found that, in some cases, the solutions were more transparent than the water present would be if there were no dissolved substance in it. Schaeffer, Paulus, and Jones[2] studied this effect of dissolved substances on the absorption of water further and found that the change in the absorption of the water was generally accompanied by a slight shift in the position of the absorption band toward the longer wave-lengths. Grantham[3] found that the alkaline hydroxides dissolved in water caused a decrease in the absorption of water at one absorption band, the effect due to these substances being greater than that due to the inorganic salts studied by the previous investigators. No conclusion can be drawn as to a shift in the position

[1] Phys. Zeitschr., 14, p. 278 (1913).
[2] Phys. Zeitschr., 15, p. 447 (1914).
[3] PHYS. REV., 18, p. 339 (1921).

of the absorption band caused by the alkaline hydroxides, since the hydroxides have an absorption band which overlaps that of water, thus making it impossible to distinguish the exact form of either absorption band. Further evidence of a shift in the position of an absorption band of water by dissolved substances was obtained by Ångstrom,[1] who measured the reflection of infra-red radiation from the surfaces of solutions. A shift in the positions of maximum and minimum reflection is interpreted as a shift in the position of the absorption band. No information was obtained as to changes in the intensity of absorption of the water.

The most intense absorption bands of water occur at about 3 μ and 6 μ. Nearer the visible spectrum there are four much less intense bands which differ greatly among themselves in intensity. These bands were located by earlier observers at about 1.0 μ, 1.2 μ, 1.5 μ and 2.0 μ, this order being also one of increasing intensity. Jones and his co-workers studied the effect of dissolved substances on the absorption of water in the spectral region including the first two of these bands. Grantham's results on the effect of the alkaline hydroxides are confined to the absorption band at 1.5 μ. Ångstrom worked in the near infra-red, but obtained results only for the intense absorption band at 3 μ.

The absorption bands of water at 3 μ and 6 μ are so intense that extremely thin layers are necessary for their study, so that a quantitative comparison of the absorption of solutions and water would be very difficult. The other four absorption bands mentioned above are such that measurable thicknesses can be used and an accurate comparison made. It was the purpose of this investigation to study the effect of various dissolved substances on the absorption of water throughout the spectral region containing these four absorption bands.

APPARATUS AND EXPERIMENTAL PROCEDURE.

It was necessary to obtain a spectrometer system free from appreciable stray radiation. Since no single spectrometer was at hand in which the stray radiation was negligible, two spectrometers were used, one serving as a monochromatic illuminator for the slit of the second. As measurements were to be made to 2.3 μ only, spectrometers with glass lenses and prisms were used. The spectrometers were of the constant deviation type and arranged as illustrated in Fig. 1.

The source of radiation, S', is a series street lighting lamp with a single spiral filament set vertically. It was run on storage batteries to insure constant current. L_1 is a lens so placed as to render the light from S' parallel. Diaphragms D_1 and D_2 were placed in the beam to

[1] PHYS. REV., 3, p. 47 (1914).

limit this beam, so that its cross-section was smaller than that of the cells under investigation. These cells were mounted on a slider P'. This slider could be moved by the observer by means of cords, so that either cell or an opaque screen was placed in the beam. L_2 is a lens which formed an image of the lamp filament on the slit S_1 of the first spec-

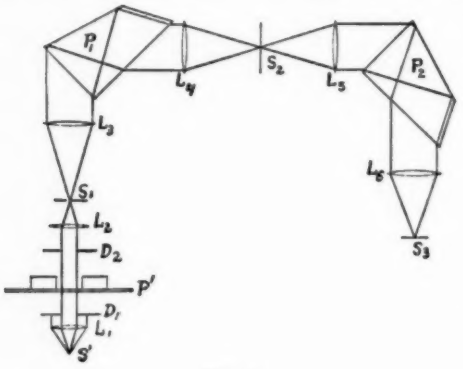

Fig. 1.

trometer. L_3, P_1, and L_4 are the collimator lens, prism, and telescope lens respectively, of this spectrometer, the spectrum being focused in the plane of the slit S_2 of the second spectrometer, of which L_5, P_2, and L_6 are the collimator lens, prism and telescope lens respectively. The spectrum is focused in the plane of the slit S_3, behind which a Coblentz thermopile is mounted. The thermopile is connected to a Coblentz ironclad galvanometer which was read by means of a telescope and scale.

The second spectrometer was used to indicate the wave-length of the radiation incident on the thermopile. The scale on the drum was divided uniformly, the smallest divisions corresponding to a range of about 0.3 $\mu\mu$ in the visible spectrum. This spectrometer was calibrated by observing the drum readings corresponding to the positions of the emission lines of sodium, lithium, potassium and mercury. The lines of the first three metals were obtained by volatilizing their salts in the open arc, and a quartz mercury arc was used for the mercury lines. A considerable number of lines were easy to locate and the location of the lines in the visible region could be checked visually. The wave-lengths of these lines were obtained from Paschen's data.[1]

The cells to contain the liquid under test consisted of two pieces of plane parallel quartz or pyrex glass between which, for the thicker cells, was placed a glass tube with plane parallel ends filled with the liquid. For the thinner cells washers of thin glass or celluloid were used. Since the two spectrometers were used in series it was necessary that the cells

[1] Ann. d. Physik., 27, p. 537 (1908).

have plane parallel ends and that the liquid be of uniform thickness over the entire cell. Otherwise a change in the direction of the beam of radiation resulted in a change in the amount of radiation reaching the thermopile even with no absorption. Thus two pieces of transparent quartz, one plane parallel and the other slightly wedge shaped, appeared to have different transmissions when placed alternately in the beam of radiation. This effect was not noticeable if the variations in thickness were not more than 0.001 cm. in a plate of 3 cm. diameter.

The coefficient of absorption of water was determined throughout the spectral region 0.8 μ to 2.3 μ by finding the absorption of known thicknesses. In order to avoid the error due to reflection at the surfaces of the cells, two cells of different thicknesses were mounted on the slider P' (Fig. 1) and the deflections of the galvanometer observed when the cells were placed in turn in the beam entering the spectrometer system. The ratio of these deflections gives the fractional transmission of a layer of water equal in thickness to the difference of thicknesses of the two cells.

The fractional transmission of the solutions was obtained by mounting on the slider P' two cells of approximately the same thickness, one containing the solution and the other containing pure water. The galvanometer deflections were observed when these cells were placed in turn in the beam of radiation. The ratio of their transmissions were thus obtained. The fractional transmission of the water could be computed from the known coefficients of absorption and then the fractional transmission of the solution calculated from that of water and their ratio. There are two advantages of comparing the transmission of the solution to that of water instead of determining the fractional transmission of the solution by using two cells of solution. First, it is the object of the experiments to compare the transmission of the solution with that of water and this method does that with one set of observations instead of two. Second, a small error in the wave-length setting of the spectrometer on the side of an absorption band will cause a large change in the fractional transmission observed if the fractional transmission of the solution is determined directly; the ratio of the transmission of the solution to that of water does not change so rapidly as we proceed along the spectrum as does the fractional transmission, hence a small error in wave-length setting does not affect the results so much.

Since the four absorption bands of water have different intensities, the cells to contain the liquid were of different thicknesses for each of the four parts of the spectral region studied. These thicknesses were: about 2 cm. for the range 0.8 μ to 1.1 μ; about 1 cm. for the range 1.1 μ to 1.3 μ; about 0.04 cm. for the range 1.3 μ to 1.7 μ; about 0.025 cm. for the range 1.7 μ to 2.3 μ.

EXPERIMENTAL RESULTS.

I. *The Absorption Spectrum of Water from 0.8 μ to 2.3 μ.*

The fractional transmission of water for known thicknesses was carefully determined throughout the spectral range studied. The agreement of the values of absorption coefficients calculated from the observed transmission of widely different thicknesses of water indicate that the apparatus was free from appreciable stray radiation. A comparison with the values obtained by Aschkinass[1] and also those calculated from the data of Jones and his co-workers[2] can be made only at the positions of maximum absorption since the wave-length calibration of the prism used by Aschkinass was apparently not correct.[3] Table I. gives the values of the absorption coefficients at these positions.

TABLE I.

Position of Maximum Absorption.	Coefficients of Absorption.		
	Aschkinass.	Jones et al.	Collins.
.97 μ	.416	.446	.448
1.20 μ	1.221	1.297	1.220
1.44 μ	38.4	——	29.4
2.00 μ	123.2	——	103

The agreement at the first two absorption bands at .97 μ and 1.20 μ is remarkably good. At the other two bands, however, the agreement is not good. The thicknesses used by Aschkinass were much smaller than those used in the present investigation and could not be measured so accurately by the method used by him. This may be a possible explanation of the differences shown in Table I.

As may be seen from Table II., the wave-lengths of maximum absorption as determined in the present investigation do not agree with those obtained by some earlier observers. The care taken in eliminating stray radiation in the present investigation may account for some of the differences in the positions of the absorption bands as compared with the results of others.

II. *The Absorption Spectra of Aqueous Solutions.*

In order to compare the absorption spectra of the solutions with that of water the amount of water in each solution was computed from a

[1] Ann. d. Physik, 55, p. 401 (1895).

[2] Loc. cit.

[3] See Coblentz, Carnegie Inst. of Wash. Pub. 65 (1906).

knowledge of the concentration and density of the solution. Then two curves were plotted on the same axes: (1) the per cent. transmission of

TABLE II.

Observer.	Date.	Kind of Prism.	Position of Maximum Absorption.			
Paschen.....	1894	Fluorspar	——	——	1.51 μ	2.05 μ
Aschkinass	1895	Flint Glass	1.00 μ	1.24 μ	1.50	1.96
Donath.....	1896	Flint Glass	——	——	1.45	1.96
Coblentz.....	1910	Fluorite	——	——	1.48	1.95
Grantham.....	1921	Rocksalt	——	——	1.48	1.98
Collins.....	1921	Flint Glass	.97	1.20	1.44	2.00

the solution as a function of the wave-length and (2) the per cent. transmission of a layer of water equivalent to that present in the solution. Four curves are plotted for each substance as different thicknesses had to be used for different parts of the spectral region studied. The thicknesses of layers used were in all cases those indicated in Fig. 3. If the dissolved substance has an effect on the absorption of the water or has an absorption of its own the two curves would not coincide. If the transmission curve for the solution lies above that for water, the dissolved substance has had an effect on the absorption of the water. If, however, the curve for the solution lies below that for the water, there are two possible explanations and in general it is impossible to separate them. It seems unlikely that the absorption bands for the dissolved substance would lie exactly at the same position and have the same shape as the water absorption band, so that the transmission curves for the solutions should be distorted from those of water if the dissolved substances have absorption bands in the region studied. An example of this is shown in Fig. 2.

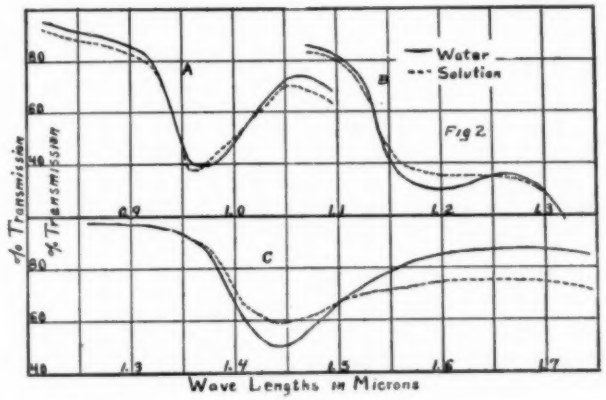

Fig. 2.

5*N* solution of NaOH. 200 grams per liter. Density 1.186 gr./c.c.

Solutions of NaOH, KOH and LiOH were studied and curves for NaOH only are shown as they are typical of the results for all three substances. Grantham has already studied solutions of these substances in the region of the absorption at 1.44 μ and showed that all of them rendered the water less absorbing in that band in spite of an absorption band of the substances themselves which overlaps that of water. Curves *A* and *B* of Fig. 2 show the effect of NaOH on water in the bands at .97 μ and 1.20 μ. At 1.20 μ there is a decided increase in the transmission but at the other band there is a decrease in transmission on one side of the band. From the distorted shape of the solution curve it was suspected that the hydroxides had absorption bands near .96 μ, 1.1 μ and 1.27 μ. Concentrated solutions were made of KOH in absolute methyl alcohol and absolute ethyl alcohol and the transmission curves determined. Absorption bands were found at the wave-lengths .95 μ and 1.1 μ and 1.26 μ. It seems safe to say then that these three alkaline hydroxides make water more transparent in all three of the absorption bands shown in Fig. 2.

Figures 3 to 15 show the results obtained for several salts, all except the last three being hydrating substances. $Al_2(SO_4)_3$, $ZnSO_4$ and the

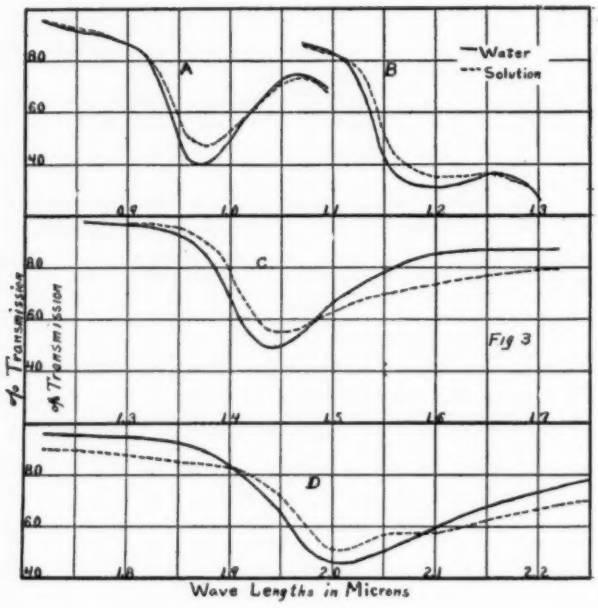

Fig. 3.

$Al_2(SO_4)_3$. 259.3 gr./liter. Density, 1.2200 gr./c.c.
Curve *A*, 2.090 cm. layer of solution. Curve *B*, .997 cm. layer of solution.
Curve *C*, .025 cm. layer of solution. Curve *D*, .0079 cm. layer of solution.

alkaline hydroxides decrease the absorption of water in all four absorption bands studied. All other substances studied decreased the absorp-

tion in the absorption band at 1.44 μ, increased the absorption in the absorption bands at .97 μ and 1.20 μ. The absorption band at 2.00 μ is not affected in the same way by all substances but in most cases where

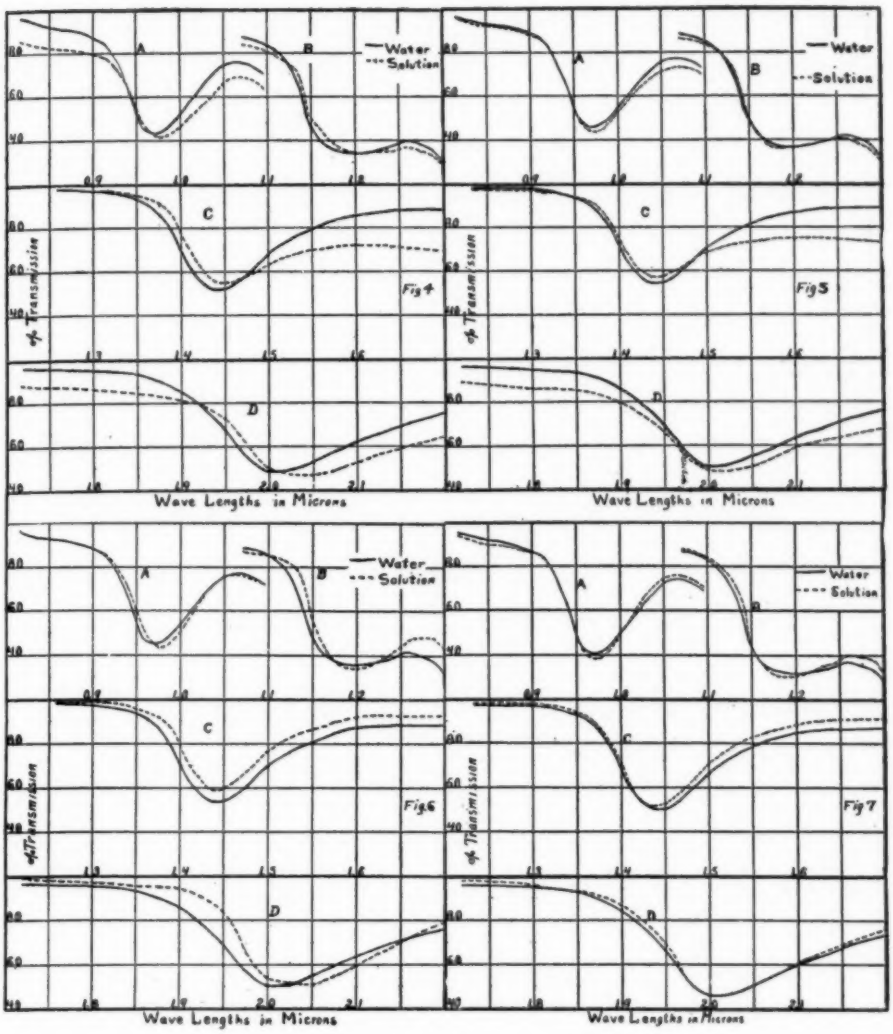

Fig. 4.

$AlCl_3$. 326.0 gr./liter. Density, 1.2133 gr./c.c.

Fig. 5.

$Al(NO_3)_3$. 430 gr./liter. Density, 1.2517 gr./c.c.

Fig. 6.

$CaCl_2$. 557.7 gr./liter. Density, 1.3950 gr./c.c.

Fig. 7.

$SrCl_2$. 296.0 grams/liter. Density 1.2445 gr./c.c.

the absorption is increased the irregularity of the curve for the solution indicates that the dissolved substance had absorption bands in this region.

No definite conclusions can be drawn as to shifts in the positions of

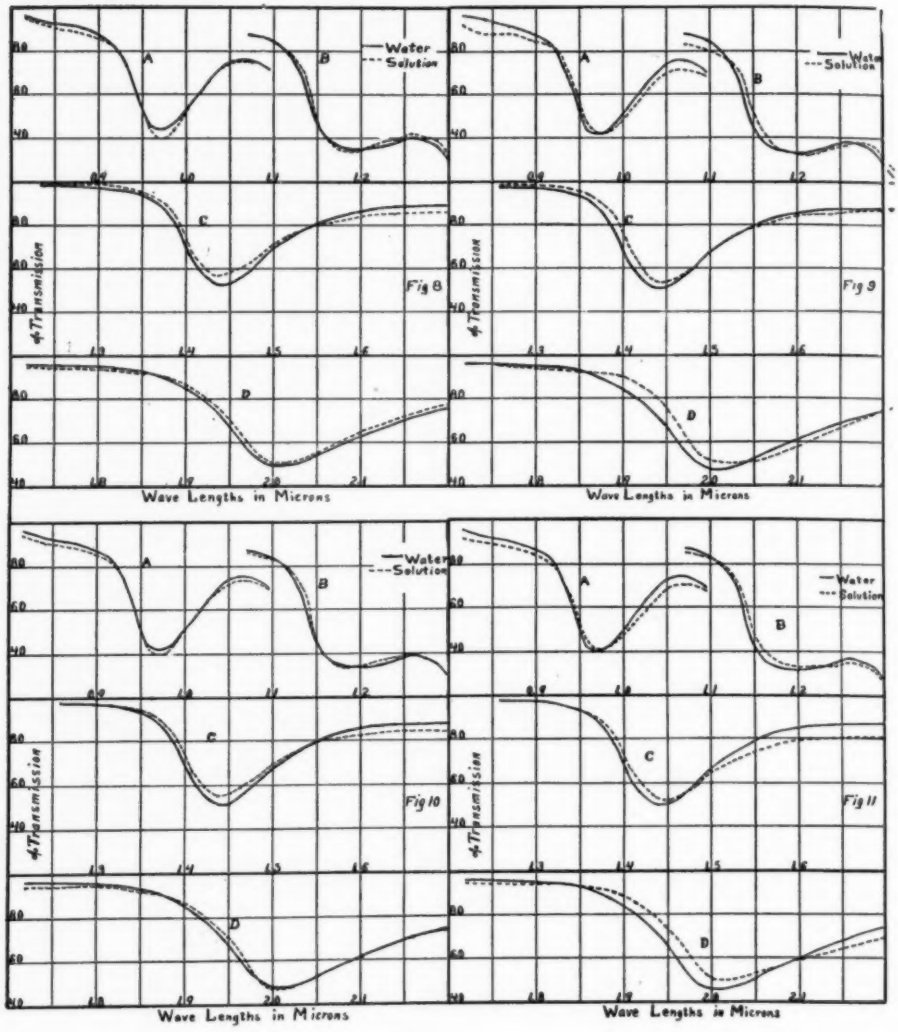

Fig. 8.

$Mg(NO_3)_2$. 424.5 gr./liter. Density, 1.2873 gr./c.c.

Fig. 9.

$MgCl_2$. 319.0 gr./liter. Density, 1.2360 gr./c.c.

Fig. 10.

$Zn(NO_3)_2$. 414.5 gr./liter. Density, 1.3200 gr./c.c.

Fig. 11.

$ZnSO_4$. 513.0 gr./liter. Density, 1.466 gr./c.c.

the water absorption bands due to the dissolved substances. In most cases where there is an apparent shift in the position of maximum absorption it is difficult to say that it is a true shift, as the presence of

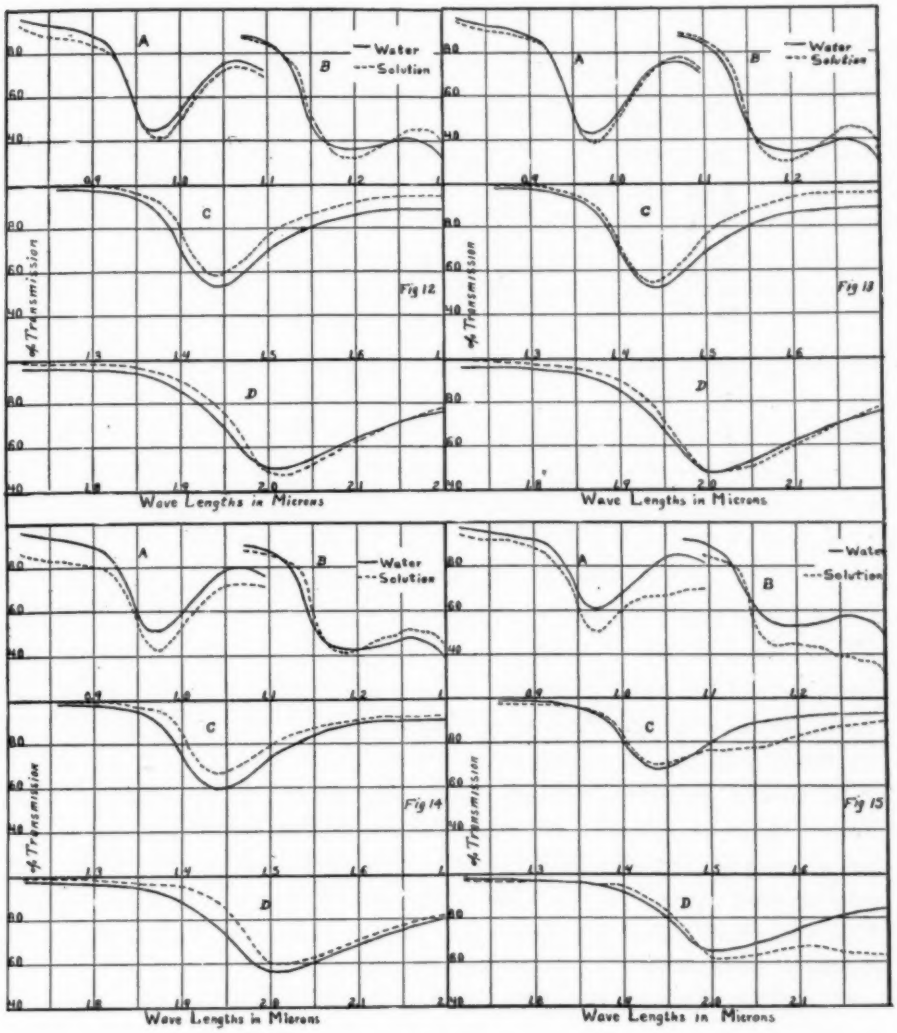

Fig. 12.

$Na_2S_2O_3$. 524.9 gr./liter. Density, 1.361 gr./liter.

Fig. 13.

NaCl. 319.8 gr./liter. Density, 1.2020 gr./c.c.

Fig. 14.

$AgNO_3$. 1413.0 gr./liter. Density, 2.1180 gr./c.c.

Fig. 15.

NH_4NO_3. 743.0 gr./liter. Density, 1.2700 gr./c.c.

an absorption band of the dissolved substance near that of the water might cause such a change in the shape of the curve.

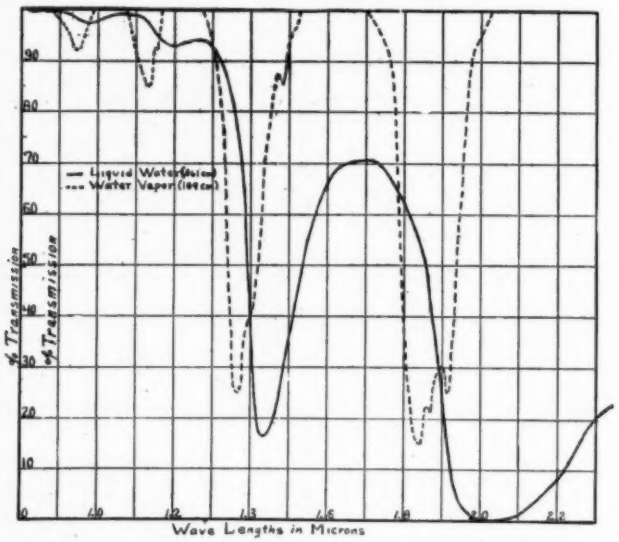

Fig. 16.

DISCUSSION.

Schaeffer, Paulus, and Jones explained their results on the basis of the solvate theory. The dissolved substances which form loose combinations with some of the water in which they are dissolved render this part of the water less absorbing. Non-hydrating substances should have no effect on the absorption of the water. Their explanation did not fit all the data which they published and does not agree with all the results shown here. $Al_2(SO_4)_3$, $ZnSO_4$, and the alkaline hydroxides make the water less absorbing at all the absorption bands, but all the remaining hydrating salts studied cause a greater absorption at some of the absorption bands. Also the three non-hydrating salts, NaCl, NH_4NO_3, and $AgNO_3$ all caused a decrease in absorption by water at one absorption band.

Livens[1] has deduced an explanation of an effect of a dissolved substance on the absorption of the solvent on the basis of the Lorentz electron theory. If the solute has absorption bands at wave-lengths much longer than that of the solvent, the solvent should absorb less than it would if the solute were absent and the position of maximum absorption should be shifted toward the shorter wave-lengths. If the solute has absorption bands at wave-lengths shorter than that of the solvent, the solvent should be more absorbing in the presence of the solute and the position

[1] Phys. Zeitschr., 14, p. 660 (1913).

of maximum absorption should be shifted toward the longer wave-lengths. This explanation would seem to lead to the conclusion that all the absorption bands of water here studied should be affected alike, as they lie close together and thus have the same relation to the absorption bands of the dissolved substance.

Neither of these explanations fits the experimentally determined facts completely. With the exceptions of $Al_2(SO_4)_3$, $ZnSO_4$ and the alkaline hydroxides, the solutes used caused an increase in the absorption of the water at the absorption bands located at .97 μ and 1.20 μ, and a decrease in the absorption of the water at the band located at 1.44 μ. From an examination of the curves it seems likely that the dissolved substances decrease the absorption of the water in the band at 2.00 μ, although in many cases this effect is apparently masked by the presence of absorption bands of the dissolved substance.

With the above exceptions then it may be said that the effect of dissolved substances is to increase the absorption of the water at two absorption bands (.97 μ and 1.20 μ) and to decrease the absorption of the water at the other two bands (1.44 μ and 2.00 μ). A parallel to this is found by comparing the absorption of water vapor and liquid water for layers having equal number of molecules. Fig. 16 shows the absorption spectra of equivalent thicknesses of water vapor and liquid water. The water-vapor curve is taken from the results of Hettner.[1] There is an absorption band in the vapor curve for each band in the liquid curve, but displaced toward the shorter wave-lengths. The absorption bands of water at .97 μ and 1.20 μ are less intense than the corresponding bands for the vapor, while the bands at 1.44 μ and 2.00 μ are more intense than the corresponding vapor bands. This fact suggests that there may be some connection between the effect of dissolved substances on the absorption of water and the effect of changing from vapor to liquid.

The fact that all the absorption bands of liquid water are present when the water is converted into vapor indicate that these absorption bands are due to the molecules and not to aggregations of molecules. Hence it seems that the only way in which the absorption could be changed to a great extent would be by a change in the number of absorbing molecules present. If there are different kinds of water molecules there is a possibility of their relative number being changed by the presence of a dissolved substance, by polymerization of the water, by change of temperature, etc. According to Langmuir's[2] model of the water molecule there may be four kinds of water molecules as the hydrogen nuclei may be

[1] Ann. d. Physik., 55, p. 476 (1919).

[2] Jour. Amer. Chem. Soc., 41, p. 893 (1919).

arranged in four different relative positions about the oxygen nucleus. These different molecules would probably have different modes of vibration which would give rise to absorption bands of different frequencies. The relative intensities of these absorption bands would depend in part on the relative number of each kind of molecule present in the water. Some such explanation together with the fact that some dissolved substances form loose combinations with the water in which they are dissolved may be able to fit the experimental results when more data are available. At present no simple explanation fits all the known results.

The writer wishes to thank Professor R. C. Gibbs, under whose direction the investigation was carried out, for his encouragement and helpful advice during its progress.

CORNELL UNIVERSITY.

THE EXISTENCE OF HIGH MOBILITY IONS.[1]

BY OSWALD BLACKWOOD.

SYNOPSIS.

Existence of Positive Ions of Abnormally High Mobilities in Air.—Contrary to the conclusions of other observers, Nolan has reported what he believes to be indications of the presence in ionized moist air of ions of eight different mobilities ranging from one to seven times the normal value. *A repetition of Nolan's experiment*, however, with duplicate apparatus, has led to an explanation of his anomalous results. In his experiment, ions generated in a small shielded space next the lower plate of a long condenser, are carried by an air current into the electric field where the mobility is determined by a blast method. At first curves similar to Nolan's were obtained, but the irregularities interpreted as due to different groups of ions were removed when precautions were taken to insure a uniform blast of air. Then it was discovered by the author that in spite of a lead shield between the emanation tubes emitting the ionizing rays and the measuring chamber, there was, contrary to Nolan's assumption, a volume ionization in that chamber, due probably to secondary x-rays from the lead, which accounted for his results. When these secondary rays were eliminated by substituting polonium as the source of ionization the mobility came out normal.

INTRODUCTION.

THE existence of small ions of very high mobility is indicated in several papers by Nolan,[2, 3] who finds a value *seven times* greater than normal. Furthermore, he detects in the ionization from radioactive bodies not *one* but *eight* widely separated sizes of ions. In so far as the writer knows, these results are at variance with the investigations of all other workers[4] who agree in assigning to the negative ion in dry and moist air mobilities 1.8 and 1.5 cm./sec. respectively. In particular, the normal value has been reported recently by Erikson[5] using a method closely resembling Nolan's.

The author has repeated the experimental work in detail, and in addition finds that the curves are capable of another interpretation and that, when certain precautions neglected by Nolan are taken, the method indicates the existence of but one size of ion of normal mobility.

METHOD.

The apparatus is fully described in Nolan's paper.[2] It consists of a shallow box 10 cms. in depth fitted with two condenser plates. The

[1] An abstract of this paper was read by title at the December meeting of the American Physical Society.

[2] Proc. Royal Irish Academy, XXXV. (A), p. 38 (1920).

[3] Ibid., XXXIII. (A), p. 9 (1916). Proc. Royal Society, XCIV. (A), p. 112 (1918).

[4] Proc. Camb. Phil. Soc., IX., p. 401. Phil. Trans., A, 195, p. 193. Annale de Chemie et de Physique, XXVIII., 289. Proc. Nat. Acad., II. (1916), 345.

[5] PHYS. REV., XVIII., p. 100 (1921).

upper (electrometer) plate is 35 cms. long and is surrounded by an earthed guard ring. The lower plate may be given any desired potential. Ionization is produced in the small trough Z below a lead shield (See Fig. 3, Z) the source being several tubes of radium emanation lying on the floor of the trough. A current of air traverses the apparatus carrying ions from Z into the condenser. When the electric field is zero these ions are carried forward horizontally. As the field is increased step by step the stream is curved upward more and more until, at a critical voltage, it is forced into contact with the upper plate and the electrometer current jumps from zero to its maximum value. In practice owing to recombination, diffusion, turbulence of the air stream, as well as other factors, the ideal curve should not be realized.

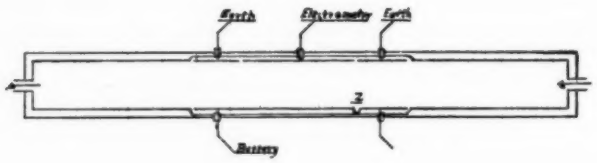

Fig. 1.

The mobility of the ions can be calculated from $u = vb^2/LV$ where V is the critical voltage at which ions begin to reach the plate, u is the ionic mobility, v the velocity of the air stream, b the vertical distance between the plates and L the plate length.[1]

Discussion of Results.

One of Nolan's typical current voltage curves for air saturated with water vapor is shown in Fig. 2. It will be noted that the curve does not cross the X axis at 14 volts as it should (1) if ions of normal mobility were present, and (2) if all the ions were produced at Z. Nolan interprets the fact that small voltages are sufficient to drive ions to the plate on the hypothesis of high mobilities. Furthermore, he explains the *eight* "nicks" or "steps" ($a \cdots f$, Fig. 2) as indicating the presence of eight different sizes of ions.

The writer has duplicated Nolan's apparatus in detail and has repeated his measurements using several different air velocities. The curves re-

[1] At the critical voltage V the ions are displaced through the vertical distance b cm. between the plates while the air stream carries them through a horizontal distance L. The electric field (potential gradient) being V/b and the vertical speed Vu/b, the time to move through the condenser is

$$t = \frac{b}{Vu/b}.$$

Also, $t = L/v$. Therefore, $u = b^2v/LV$.

semble those of Nolan in that they pass through the origin, showing that small fields are sufficient to drive ions to the plate. They also have "nicks" or "steps" but these are not repeatable and are probably due to lack of constancy in the motion of the gasometers used to force air through the apparatus. After these gasometers were replaced by a constant-speed rotary pump the curves showed no irregularities. They show no evidence, therefore, of the existence of separate, distinct groups or sizes of ions.

The first inkling of an explanation of the form of the curve not involving the assumption of high mobilities came when the air stream in the ion box was reversed in direction. If all the ions were really produced in the shielded space *Z*, as Nolan assumed, this procedure should reduce the galvanometer current to zero, since the reversed air stream carries the ions *away* from the condenser. In fact, however, the current decreased only one third. Most of the ions, therefore, are produced in the main volume of the condenser.

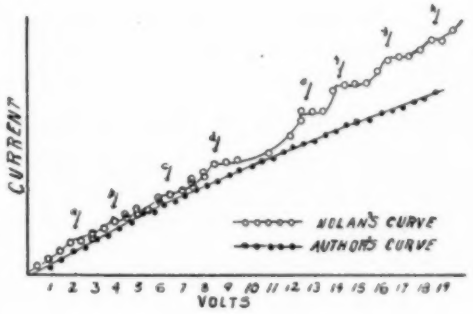

Fig. 2.

The distribution in still air of this general ionization has been studied as follows. A wire screen of 1 cm. mesh was placed horizontally between the two condenser plates. (See Fig. 3, *X*.) It was charged to the

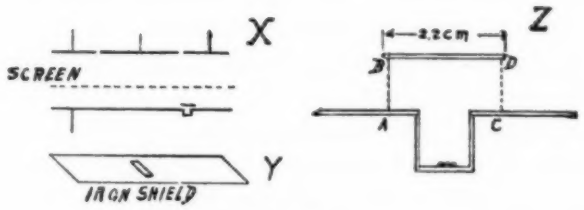

Fig. 3.

same potential as the lower plate so that no ions produced below it should be driven to the electrometer. The potential of the screen was given a sufficiently high value to drive all ions above it to the electrometer plate. The current was found to be directly proportional to the distance between the screen and plate. This indicated a uniform vertical distribution of the ionic density. Therefore, the ionization near the electrometer plate is as great as that in the lower part of the condenser. This being the

case, an explanation of the experimental curve is simple. Ions are driven to the upper plate by small fields not because the ions have *high mobilities, as Nolan assumed*, but because they are generated in *immediate proximity* to it.

SOURCE OF GENERAL IONIZATION.

With the purpose of discovering the source of this general ionization, its horizontal distribution in still air was investigated. The wire screen described above was replaced by a grounded sheet of iron which was fitted with an aperture four cm. wide. (See Fig. 3, *Y*.) This sheet of metal shielded the electrometer plate from all ions which were not generated immediately below the slit. Keeping the electric field constant, the sheet was shifted horizontally so as to successively uncover all portions of the upper plate. The electrometer currents for the various positions show that more than one third of all the ions are produced at distances from the ion trough *Z* greater than 10 cm.

In order to investigate the absorption of the rays causing the general ionization, the window *CD* (Fig. 3, *Z*) was blocked with a lead plate while *AB* was covered with a paper screen found to be equivalent to .001 cm. thickness of aluminium foil. This shield decreased the ionization about 50 per cent. Replacing the paper by a sheet of lead 1 mm. thick reduced it to zero. Since the window *CD* is shielded from direct radiation, and since the paper was adequate to prevent diffusion of ions into the main chamber, by elimination it seems probable that the general ionization was due to secondary Roentgen radiation from the lead walls of the trough at *Z*. While this radiation is doubtless relatively feeble, the volume of air penetrated by it is at least one hundred times that of the volume at *Z* which is subject to direct radiation.

An attempt was next made to eliminate secondary radiation and realize experimentally the intense, localized ionization which Nolan assumed to exist in his apparatus. The ionizing agent used was polonium which emits only alpha rays. The specimen was equivalent in ionizing power to about 1/40 mg. of radium bromide. With an air velocity of 4.1 cm./sec., several current-voltage curves were determined of which Fig. 4, *A*, is typical. This curve has only one break in slope corresponding to a critical voltage 7.5 and a mobility 2.15 cms./sec. It will be noticed that a considerable number of ions are driven to the plate at voltages less than 7.5. This was attributed to turbulence of the air stream and to secondary radiation. To decrease the former the height of the ion box was reduced fifty per cent., thus increasing the ratio of length to cross section. To lessen secondary radiation the shield over *Z* was

lowered 5 millimeters thus decreasing the size of the openings through which the radiation might pass. Using the modified ion box only two curves were determined. (See Fig. 4, *B*.) The intercepts are much more sharply defined than in the case of the preceding curve. The com-

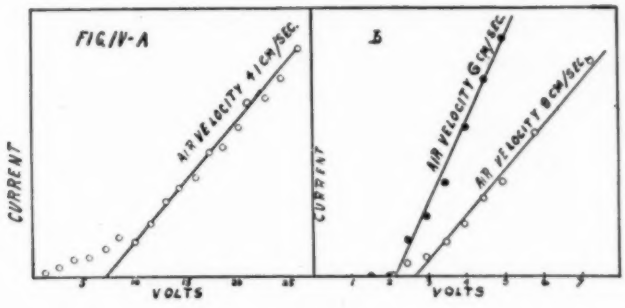

Fig. 4.

puted mobilities, 1.96 and 2.13 cm./sec. are respectively within 30 and 42 per cent. of the accepted value for moist air. The agreement is not close, but it is sufficient to show that the method indicates the existence of only *one size* of ion of approximately normal mobility.

Summary.

1. Nolan has presented evidence indicating the existence of several sizes of high-mobility ions.

2. The writer, after duplicating the apparatus, finds no evidence for the existence of several groups.

3. General ionization, proved to exist in the tube, is adequate to explain the experimental curves. It is not necessary, therefore, to assume the existence of high mobility ions.

4. After eliminating general ionization, the method gives approximately the mobility value found by other workers.

Note Added October 10, 1922.

Further evidence as to the existence of the ions of high mobility has been reported by Nolan and Harris.[1] After adopting a more accurate alternating-field method, *they find no trace of the mobile ions*. The writer believes that this confirms his own results, but Nolan and Harris explain the failure to detect the ions on the assumption that in the new apparatus the ions recombine before reaching the electrometer plate. They write as follows:

"We think that the explanation lies in the one radical difference between the two methods. In the air-current method the ions of one

[1] Proc. Royal Irish Acad., Sect. A, XXXVI., p. 31, 1922.

sign are almost immediately separated from those of opposite sign and for practically all their path in the measuring vessel are moving through air free from other ions. In the alternating-field method the ions are in contact with one another for some time in the space above the perforated plate. The time that an ion spends in this space will depend upon the value of the field there, the distance from the place where it is formed to the perforated plate, and its mobility. . . .

"It seems to us reasonable to suggest that the alternating-field method fails to reveal the faster ions because they have disappeared by recombination. The older method does reveal them because the chances of recombination have been reduced to a minimum."

This explanation will be shown to be quite inadequate since the ions in the older method are by no means "immediately" removed from those of opposite sign. Indeed, the time available for recombination is actually much greater in the older apparatus. In this method the ions are produced in the space immediately below a lead plate 2.2 cms. wide (Fig. 1, *Z*), and are not subject to the electric field and, consequently, are not separated from those of opposite sign until they have moved forward an average distance of at least 1.1 cms. The air velocity being 6 cm./sec., the time available for recombination is at least 1/5 second. In the newer apparatus the ions after being produced in a box 4 cms. high are driven downward toward a perforated plate through which they pass into the condenser proper. Until they reach this plate they are in contact with ions of opposite sign and are subject to recombination. The mean distance to the plate is thus 2 cms., the field strength was 4 volt/cm. and the time available for recombination for the three fastest ions (mobilities 12, 7, and 4 cm./sec.) would be respectively 1/24, 1/14, and 1/8 seconds. Thus the times available for recombination were respectively 1.6, 3, and 5 times greater in the older apparatus than in the new.

After failing to detect the ions in moist air, Nolan and Harris next introduced a new condition by drying and, using the new apparatus, found an abundance of faster ions. These results, however, must be regarded with caution since they are quite opposite to those of Loeb,[1] who also used an alternating-field method. He dried the air so thoroughly that free electrons were detectable for several days, but found no trace of abnormally mobile ions.

THE UNIVERSITY OF PITTSBURGH,
DEPARTMENT OF PHYSICS,
PITTSBURGH, PA.

[1]PHYS. REV., XVIII., p. 89, 1921; XVIII., p. 633, 1916. Nat. Acad. Sci. Proc. (6), p. 435, 1920.